

Formation, Phase Equilibrium and Gas Exchange of Methane Hydrates

Hao Bian

A thesis submitted in partial fulfilment of the requirements for the degree of
Doctor of Philosophy in Chemical Engineering of Imperial College London and
the Diploma of Imperial College London

Department of Chemical Engineering
Imperial College London
London SW7 2AZ, United Kingdom

June 2017

Originality Declaration

I herewith certify that all material in this dissertation which is not my own work has been properly acknowledged.

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Acknowledgements

Firstly, I would like to express my gratitude to my academic supervisors, Professor Geoffrey C. Maitland, Professor Klaus Hellgardt, and Dr. Jerry Y. Y. Heng for providing such excellent mentoring during my PhD study. The work would not have been possible without your constant guidance, support, and thoughtful inputs. I would like to express my deepest gratitude to Professor Geoffrey C. Maitland, who initiated my PhD project and secured funding for my project. Your dedication in science, your thorough ideas, and your committed supports have influenced every success during the study and in the future. Since I embarked on the PhD project, I was fortunate enough to be allowed to explore a variety of ideas, which lay as the building blocks of the future research pyramid. I would like to acknowledge Professor Eric May and Dr. Paul Stanwix who accommodated and facilitated my research secondment at University of Western Australia. I would like to thank electrical and mechanical workshop staff, especially, Gavin Barnes, Richard Wallington, and Chin Lang for your professional support and the help I received during the project.

I thank all the friends and colleagues at Imperial with whom I spent the last unforgettable four years, including Cheng Peng, Rayane Hoballah, Shane Cadogan, Claudio Calabrese, Tao Li, Kai Liu, Bing Tian, Zili Zhang, Ziran Da, Yan Wang, Weparn Julian Tay, Lorena dos Santos de Souza, Yolanda Sanchez-Vicente, Theodor Videnberg, Sultan Al-Habsi, Benaiah Anabaraonye, Mihaela Stevar, Chidi Efika, and many others. Thank you for making this chapter of my life enjoyable.

Lastly, I would like to extend my utmost gratitude for the support I received from my wife and my parents, whose love encouraged me to overcome challenges and difficulties during the journey. This thesis would not have been possible without your deepest love and care.

At the end, my favorite quote is:

“I hope this work is not the end of the fundamental measurements. I hope the last sentence is not just a hope.”

Hao Bian

June 2017

Abstract

The phase behaviour and the formation/gas exchange kinetics of methane hydrates have been studied at elevated pressures and low temperatures, conditions under which naturally occurring hydrates exist or synthetic gas hydrates are formed during exploration operations and transportations. To this end, experimental measurements of hydrate phase equilibria for the binary methane and water mixture were made in mesoporous and macroporous silica, a stirred slurry reactor was used to study hydrate formation kinetics under various driving forces and water-based media, and a new Raman imaging technique was devised to study the exchange kinetics of methane hydrates with carbon dioxide under reservoir conditions.

The formation kinetics of methane hydrates were measured using a high-pressure low-temperature autoclave system with a special focus on (a) the physical state of the water phase from which hydrate is formed and (b) the effect of available gas-water interfacial area for mass transfer and reaction during gas hydrate formation. The initial formation rate of methane hydrates in an agitated binary methane and water system was shown to have a universal exponential dependence on the driving chemical potential difference at temperatures between 276.5 K and 283.5 K and pressures between 5 MPa and 10.5 MPa. The hydrate formation rate was also studied for a methane-micronised ice particle system and a methane-‘Dry Water’ system consisting of a nanoparticle-stabilised high internal volume ‘dry’ water emulsion. The results indicated that the large differences in reactive surface area and gas diffusion rates for these three different pre-cursor systems resulted in pronounced effects on the initial formation rate of methane hydrates. Physical mechanisms were proposed to rationalize the observed behavior; it is anticipated that the results could be used to predict the hydrate formation rate for different combinations of water precursor state, reaction geometry and agitation conditions.

As a model for natural gas hydrates formed in porous mineral sediments, the phase equilibrium behaviour of synthetic methane hydrates were measured, using high-pressure differential scanning micro-calorimetry, in mesoporous and macroporous silica that had controlled pore

sizes ranging from 8.5 nm to 195.7 nm. The effect of pore surface chemistry was also qualified by studying the phase equilibrium in surface functionalised porous media. An oscillating dynamic method was used to essentially fully convert the ice/water pre-cursor into hydrates followed by slow heating in the micro-DSC to determine the decomposition conditions of methane hydrates in the porous silica over a wider range of pressures and pore sizes than previous studies. Significant shifts in dissociation temperatures with pore size were observed and rationalised using a modified Gibbs-Thomson equation. The experimental data up to 50 MPa indicated that the confinement effect in porous media showed a significant pressure dependency, most likely due to the interfacial energy. The effects of interfacial energy on the phase equilibria were investigated quantitatively by grafting different chemical groups onto the silica surface. The dissociation temperatures of methane hydrates in hydrophilic and hydrophobically-modified silica pores were significantly different; hydrates in strongly hydrophobic porous silica tended to behave like bulk methane hydrates regarding the melting temperature, with no significant effect of confinement. The measured phase equilibria, interfacial energy and enthalpy data can be used as parameters in gas hydrate simulation models.

For the Raman studies, a high-pressure low-temperature optical reactor was designed, commissioned and applied. The cell accommodated samples to be analyzed over a temperature range of 288 K to 353 K and at pressures up to 50 MPa. Fast temperature response (up to 5 K/s), and stable temperature control (± 20 mK) were facilitated by using four Peltier elements. A large optical path allowed the acquisition of *in-situ* 3D Raman images to reveal the molecular structure and (CH₄-CO₂) exchange kinetics of gas hydrates in both single crystal and polycrystalline methane hydrates. An oscillating dynamic method was used to form polycrystalline hydrates at pressures up to 15 MPa and by contrast single crystal hydrates were formed under a small thermal driving force (around 3 K) at pressures up to 14 MPa. The polycrystalline hydrates exhibited a much faster CH₄-CO₂ exchange rate compared to the single crystal hydrates; defects and crystal imperfections also had a significant effect on this rate. The morphology of methane hydrates hence plays a critical role in the exchange process, which helps to explain the discrepancy of exchange rates for similar conditions reported in the

literature. These time-resolved Raman results indicated a diffusion-controlled guest molecule substitution process. The Raman spectra were also used to quantify the exchange kinetics and the cage occupancy of the methane hydrates.

This work has provided new insight and data for the rate of methane hydrate formation, their phase behavior under confinement and rates of gas exchange as a function of hydrate physical state under pressure and temperature conditions relevant to natural gas hydrate systems and their potential exploitation. The research represents a significant step forward in our fundamental understanding of the way gas hydrates are formed and behave. The collected data and derived parameters offer valuable inputs to process simulators concerning field exploration/production and potential uses in gas transportation and separation. Areas in which the research could be usefully extended have been identified.

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Chapter 1 Introduction

1.1 Introduction

In 2014, the global primary energy use had increased by 20% from 2004; the energy use pattern in 2014 was oil (31%), coal (29%), natural gas (21%), biofuels (10%), nuclear (5%), and other renewables (4%), with fossil fuels counting for 81% share of the total energy use. It is projected that the energy demand will continue to increase by 48% between 2012 and 2040, with the main demand coming from fast emerging economies like China and India [1]. Consumption of fossil fuels leads to emissions of greenhouse gases (GHGs), which cause global warming and climate change [2]. To mitigate the potential impacts of climate change, the 21st Conference of the Parties (COP 21) agreed to limit the temperature increase to under 2 °C compared to pre-industrial levels [3]. Such limits can be achieved by energy efficiency improvements, the adoption of best available technologies (BATs), resource efficiency measures, and, more importantly, through a significant reduction in the share of fossil fuels used in global energy production [4]. Natural gas, which emits less carbon dioxide (CO₂) than other fossil fuels per unit energy, may act as a bridging fuel during the transition from oil dependency to new technologies that will eventually replace fossil fuels [5]. New technological advancements, like hydraulic fracturing and horizontal drilling in shale formations, allow the oil and gas industry to develop unconventional resources, making natural gas hydrates the next promising energy resource to be developed [6].

The technological interest in gas hydrates began in 1934 when gas hydrates were found blocking pipelines during gas transportation and recovery [7]. In 2010, gas hydrates were blamed for the failure of a 100-ton containment structure that was aimed at stopping the Macondo well blowout in the Gulf of Mexico [8]. Naturally occurring gas hydrates are also a widespread source of methane (CH₄), found typically under permafrost and in the continental margins. The most conservative estimates indicate that the energy contained in natural gas hydrates (10¹⁶ m³ of CH₄ at STP*) is more than that of all conventional fossil fuels added together [9]. Therefore, one can say that natural gas hydrates have the potential to meet the increasing energy demand and serve as a long-term bridging fuel for the future.

* STP: Standard temperature and pressure

1.2 Scope and Objectives

To assess properly the energy potential of natural gas hydrates, accurate quantification of methane hydrates is essential [10]. Methane hydrates are usually distributed in porous soft sand-clay sediments. These ‘hydrate crystal’ deposits constitute an increasingly favoured target for future energy production [11]. However, most thermodynamic studies of gas hydrates have been carried out on bulk hydrates rather than under confined conditions. Understanding the confined phase behaviour is therefore fundamental to devising safe and cost-effective processes to extract gas from these hydrates.

Ideally, thermophysical properties are obtained from naturally occurring hydrate samples. Although pressure coring techniques allow intact core samples of natural gas hydrates to be recovered [12], *in-situ* testing methods are still unavailable. Consequently, synthetic hydrates are required for a variety of laboratory tests. A better understanding of formation kinetics and mechanism of hydrates is demanded to synthesise hydrates for different analysis, i.e., hydrates with different morphologies and confined hydrates.

A few production methods have been proposed to recover methane from natural gas hydrates, including depressurisation, heat stimulation and chemical injection, all of which are involved in the destabilisation of the methane hydrate structure [13]. Such processes can be accompanied by geological and environmental hazards, landslides, tsunamis and the release of greenhouse gases [14]. The recovery of methane hydrates by carbon dioxide injection is a promising route for long-term storage of CO₂ and producing methane from natural gas hydrate reservoirs without altering their geological stability. Some progress has been made in understanding the fundamental aspects of this process [15]. However, the microscopic exchange mechanism is still a subject of debate [8].

The main objectives of this research can therefore be summarised as follows:

- I. To synthesise fully converted methane hydrates in the laboratory, (a) to understand hydrate formation kinetics with a special focus on (i) the physical state of the water phase from which hydrates are formed and (ii) the effect of available gas-water interfacial area for mass transfer and reaction during gas hydrate formation; (b) to

form hydrates in model porous media for phase equilibrium studies; (c) to form bulk hydrates with variations in morphologies.

- II. To study phase equilibrium conditions of methane hydrates in porous media under a wide range of temperatures and pressures, and identify key parameters (e.g., surface chemistry of porous media) that affect the confined melting points.
- III. To design a high-pressure optical reactor that is suitable for *in-situ* measurements of hydrate properties at high pressure with accurate temperature control at low temperatures. The cell should have an optical window for laser and optical measurements; moreover, the size of the cell should be compatible with confocal Raman microscopes.
- IV. To use the Raman imaging technique to study exchange kinetics of methane hydrates with carbon dioxide and investigate the effect of different hydrate morphologies.

1.3 Thesis Outline

Chapter 2: A review of the background on gas hydrates—including key properties, the geological settings, and field production tests of natural gas hydrates—is presented in this chapter. Different techniques used to synthesise methane hydrates in laboratories are also discussed therein.

Chapter 3: The results on the formation kinetics of methane hydrates—measured in a high-pressure low-temperature autoclave system with a focus on the physical state of the water and interfacial area of the precursors—is described in this chapter.

Chapter 4: The investigation of the phase equilibrium behaviour of confined methane hydrate in porous media with controlled pore sizes—using a high-pressure differential scanning micro-calorimeter—is described. The dissociation temperatures of methane hydrates in hydrophilic and hydrophobically-modified silica pores have been measured as well.

Chapter 5: The design, fabrication, and testing of a unique optical cell for Raman spectroscopy and imaging studies of multiphase systems, including gas hydrates, is described in this chapter.

Chapter 6: The kinetic study on CH₄-CO₂ exchange of gas hydrates—using state-of-the-art Raman spectroscopy with *in-situ* 3D imaging capabilities, emphasising the effect of hydrate morphologies—is presented in this chapter.

Chapter 7: Conclusions from each chapter, identifying the key contributions from this work, are summarised in this chapter. Areas to which the research could be usefully extended are also covered

Chapter 2 Background to Gas Hydrates

2.1 Overview

Gas hydrates are ice-like solid compounds in which gas molecules are enclosed within water cages, called ‘clathrates’. They are stable under high pressures and low temperatures [16]. Although there has been scientific interest in gas hydrates since Priestley’s discovery of sulphur dioxide hydrates in 1778 [17], technological interest in them increased with concerns about flow assurance issues, whereby they form inside and block subsea pipelines when natural gas is transported and recovered. During recent decades, research efforts have been made to understand the potential of using naturally occurring methane hydrates as an alternative energy source [8]. The development of understanding gas hydrates can be divided into three periods [16].

- The first period is from 1778 to present. Since the discovery of gas hydrates, scientists have contributed numerous efforts to identify all components that are capable of forming gas hydrates. Meanwhile, the quantitative properties of gas hydrates, including phase behaviour, density, thermal conductivity and other thermophysical properties, have been measured.
- The second period is from 1934 to present. In 1934, Hammerschmidt identified gas hydrates as the culprit for a winter blockage during the transportation of natural gas in the presence of water vapour [7]. Since then, methane hydrate inhibitors have been intensively studied. Various thermodynamic and kinetic inhibitors of methane hydrates were examined to mitigate potential flow assurance hazards caused by gas hydrates during hydrocarbon drilling, processing, and transportations. The worldwide costs of methanol for hydrate inhibition have been estimated at USD\$ 200 million annually [18].
- The third period is from 1969 to present. Naturally occurring methane hydrates were first found by Russian scientists when they were searching for gas reservoirs [19]. Since then, significant progress has been made in systematically accessing the geologic occurrence

of gas hydrates in nature. During the last decade, the execution of methane hydrate field production tests demonstrated the possibility of producing natural gas from methane hydrate reservoirs despite the shortcomings in economic feasibility with current production technologies [20].

Today, gas hydrate research essentially covers a combination of the aforementioned three areas [16]. National gas hydrate programmes, along with scientific and industry interest, have led to numerous advances in gas hydrate research [21]. This chapter introduces the fundamental properties of gas hydrates. The occurrence, depositional conditions and production methods of naturally occurring methane hydrates are reviewed as well. Furthermore, the formation methods of gas hydrates are also described.

2.2 Properties of Gas Hydrates

2.2.1 Structure of Gas Hydrates

The structure of gas hydrates is defined by the cavities assembled by water molecules. According to the types of the cavities, there are three common types of gas hydrates, known as Structure I (sI), Structure II (sII), and Structure H (sH), also known as Type I, Type II and Type H [22]. Type I hydrates occur in nature, whereas Type II and Type H hydrates are man-made hydrates [18]. Figure 2.1 shows the structure of different types of gas hydrates.

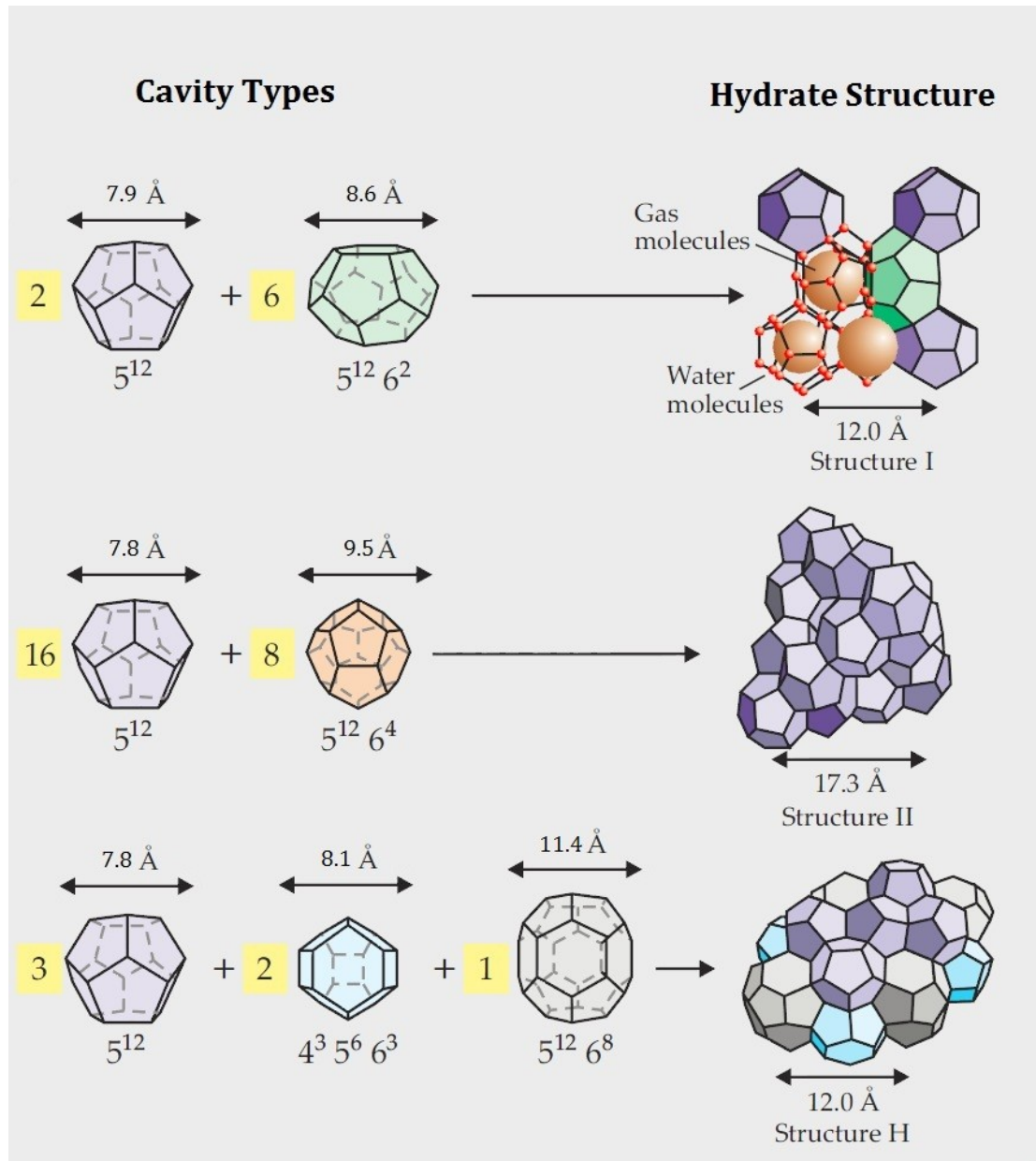


Figure 2.1 Structure of gas hydrates “Reproduced from Mao et al. [23], with the permission of the American Institute of Physics.”

Figure 2.1 illustrates the three different structures of gas hydrates. Dodecahedron and tetrakaidecahedron water cages with a ratio of one to three make up the structure I hydrates. The dodecahedron cage consists of twenty water molecules, which are connected by hydrogen bonds to form twelve pentagonal faces (denoted by 5¹²). Another type of tetrakaidecahedron cage is made of twelve pentagonal faces and two hexagonal faces, which contain twenty-two water molecules in a unit structure (denoted by 5¹² 6²). The dimensions of dodecahedron and tetrakaidecahedron cages are 7.9 Å and 8.6 Å (note that Å equals to 0.1 nm), respectively [23].

Structure H was firstly introduced by Ripmeester in 1987 [24]. Structure H hydrates require small molecules (e.g., methane) and large structure H formers. As the molecular sizes of most structure H hydrate formers are larger than the small cages, these molecules, such as t-butyl-methyl-ether, tetramethylsilane, hexachloroethane and adamantane only occupy the large cages. Other small gas molecules such as methane and nitrogen can occupy the 5^{12} and $4^35^66^3$ cages. Although structure H hydrates are less likely to be found in nature, they are still of interest because those large molecules only occupy the large cages and leave the small cages empty for small molecules to accommodate, indicating theoretical possibilities of gas storage and gas separations [16, 25].

2.2.2 Guest Molecule Size of Gas Hydrates

More than 130 compounds, also called guest molecules, are known to form clathrate hydrates [16]. The size of guest molecules, ranging from 3.8 Å (Krypton) to 7 Å (n-butane), is governed by the structure of the clathrate hydrates. Molecules that are smaller than krypton, such as helium, are too small to be stabilised in the water cages and held in place by the van-der-Waals forces between the guest and surrounding water molecules. Molecules which are larger than n-butane, such as pentane, hexane, and paraffin, are too large to be incorporated into the clathrate cages of Type I and Type II hydrates. These large molecules can form Type H hydrates, but the upper limit of the guest molecule size is around 9 Å [22]. Figure 2.2 illustrates the relationship between guest molecular sizes and different types of hydrates.

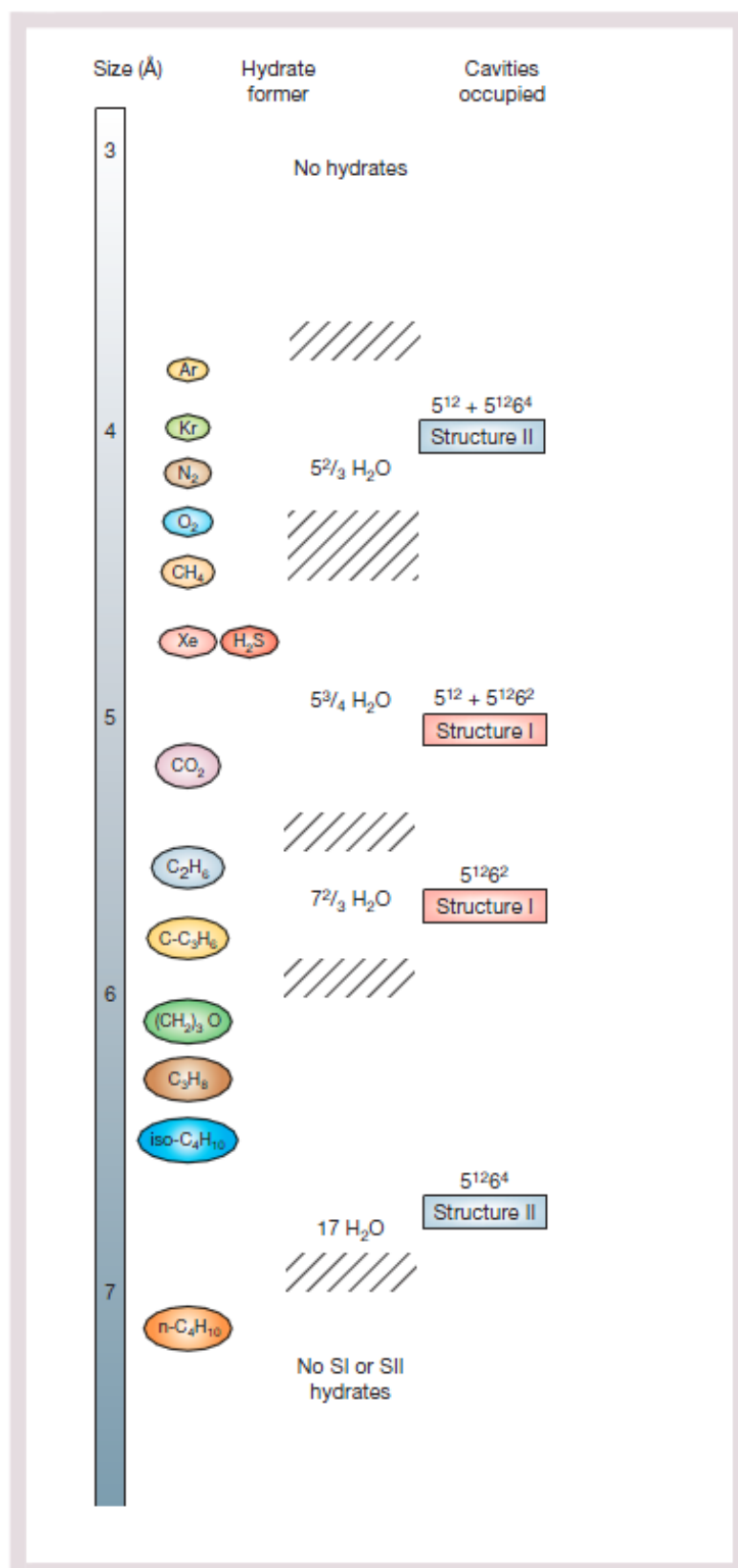


Figure 2.2 Guest molecules and the sizes of Structure I, Structure II and Structure H hydrates.
 “Reprinted by permission from Macmillan Publishers Ltd: Sloan [18], copyright (2003)”

With the development of research techniques (e.g., Diamond Anvil Cells), extreme conditions such as ultra-high pressure up to 3 GPa become achievable [26]. Some literature reported that hydrogen could form Type II hydrates under ultra-high pressures (ca. 200 MPa) [27]. Meanwhile, methane hydrates have been classified as Type I hydrates for many years. However, recent research showed that under high pressures (above 250 MPa), methane hydrates were partially converted to Type II hydrates [28]. Apart from the three common hydrate structures, Structure T hydrates were firstly introduced by Udachin and co-workers [29]. The Structure T clathrate hydrates, occupied by dimethyl ether as guest molecules, consist of three types of cages ($5^{12}6^3$, $5^{12}6^2$, and $4^15^{10}6^3$). Other unusual clathrate structures were reviewed by Sloan and Koh [16].

2.2.3 Key Properties of Gas Hydrates

The three common clathrate hydrates consist of around 85 mol% of water molecules, suggesting that the mechanical properties of gas hydrates should be similar to those of ice (Ih). However, due to the addition of guest molecules in the hydrate structure, the thermal properties of hydrates are distinct from those of ice [30]. Table 2-1 summarises key properties of gas hydrates and ice.

Table 2-1 Comparison of Properties of Ice (Ih), Structure I, and Structure II Hydrates [16].

Property	Ice (Ih)	Structure I	Structure II
Water molecules number ^a	4	46	136
Lattice parameters at 273 K (nm)	a=0.452, c= 0.736	1.2	1.73
Compressional velocity, V_p (m·s ⁻¹)	3870.1	3778.0	3821.8
Shear velocity, V_s (m·s ⁻¹)	1949	1963.6	2001.1
Linear thermal expansion at 200 K (K ⁻¹)	56×10^{-6}	77×10^{-6}	52×10^{-6}
Specific heat capacity (J·kg ⁻¹ ·K ⁻¹)	1700 ^b	2080 ^b	2130 ^b
Thermal conductivity at 263 K (W·m ⁻¹ ·K ⁻¹)	2.23	0.49	0.51
Density (kg·m ⁻³)	916	940	1291 ^c

a, per unit cell; b, Ice Ih at 248–268 K; CH₄, sI at 253–288 K; THF, sII at 248–265.5 K

c, 2,2-dimethylpentane·5(Xe, H₂S)·34H₂O

d, all properties listed are temperature(pressure) dependent except for water molecules number

Gas hydrates, especially CH_4 hydrates, are normally synthesised from granulated ice. Submicron pores and macro voids, as shown in Figure 2.3, exist inside and between hydrate grains [31]. The porous nature of gas hydrates complicates the measurements of bulk properties, for example, densities and thermal conductivities. To mitigate the influence of the porous morphology, Helgerud and co-workers [32] applied high compressions (up to 105 MPa) to hydrates that formed from granulated ice and an annealing process via various stages at temperatures between 253 K to 288 K to minimise the impact of porosities on subsequent measurements. Single crystal methane hydrates were also synthesised under ultra-high pressures (ca. 1 GPa) in aqueous phase (water) using Diamond Anvil Cells (DACs). The resulting methane hydrate crystals were 300 μm to 500 μm in diameter [28, 33, 34]. Such crystals could be potentially used for further tests but are limited by the geometry of DACs and the aqueous pressure medium.

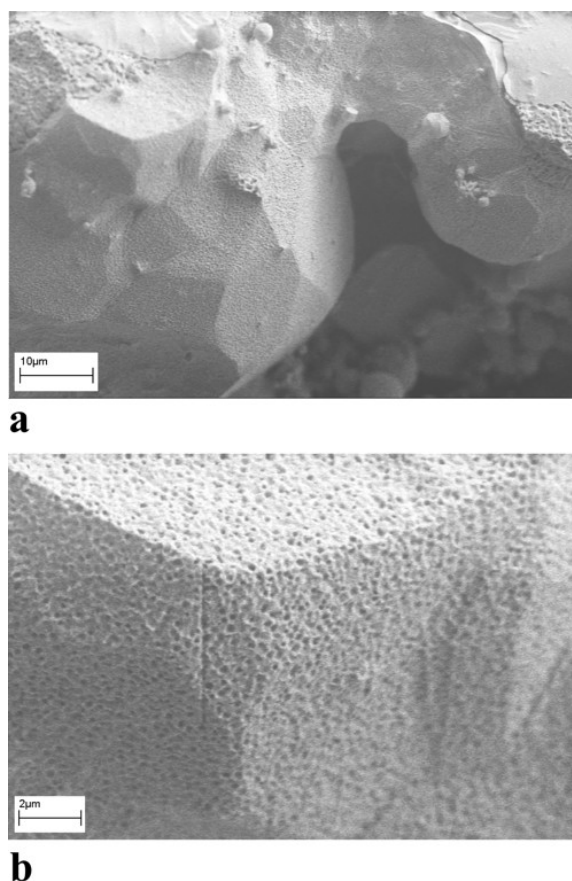


Figure 2.3 Field-emission scanning electron images of CH_4 hydrates synthesised from ice. Gas hydrates with size around 30 μm show the facets of hydrate crystals (a) and submicron porous structure of CH_4 hydrates (b). “Reprinted with permission from Staykova et al. [31]. Copyright (2003) American Chemical Society.”

When hydrates are converted into water and gas, the enthalpy change is defined as the heat of dissociation (ΔH_d), which is related to the number of hydrogen bonds in the clathrate structure. The heat of dissociation of hydrates is relatively constant with a range of guest molecules that are incorporated in the same hydrate cavities (shown in Table 2-2).

Table 2-2 Heat of fusion for various hydrates [35]

Guest molecules	Structure	ΔH_d (kJ/mol-gas)	ΔH_d (kJ/mol-water)
Methane	sI	54.2	9.03
Ethane	sI	71.8	9.36
Propane	sII	129.2	7.60
Isobutane	sII	133.2	7.84
Ice	Ih	-	6.01

The formation of gas hydrates is exothermic, and heat is released. Conversely, the dissociation of methane hydrate is an endothermic process. The difference between ΔH_d of hydrates and ice is caused by the additional van-der-Waals forces between guest molecules and surrounding water molecules.

The three-phase equilibrium (H-L_w-V) pressures, shown in Figure 2.4, have an exponential dependence on temperature [30]. The equilibrium also depends on the ratio between guest molecule size and cavity size. In other words, the equilibrium conditions are set by the type of hydrate structure and the guest molecules [16].

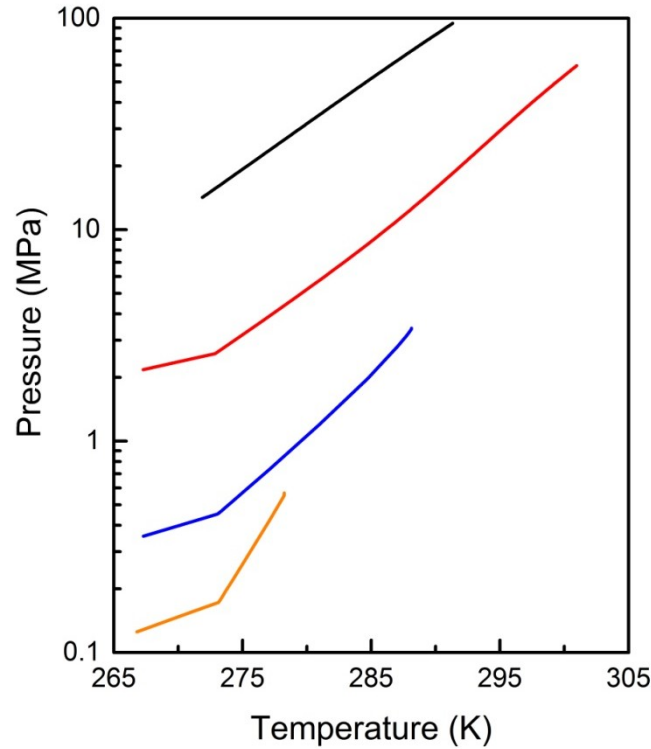


Figure 2.4 Phase equilibrium of typical hydrates. (Data obtained from Multiflash 6.0 software).

— Nitrogen, — Methane, — Ethane, — Propane

2.3 Naturally Occurring Methane Hydrates

2.3.1 Widely Distributed Potential Energy for the Future

Natural gas hydrates, as a potential energy source, have attracted the world's attention mainly due to two factors, the tremendous amount potentially available and the wide global distribution along the continental margins and in permafrost [36].

Since the discovery of naturally occurring methane hydrates in the early 1960s, estimations of the total amount of natural gas hydrates have been controversial over the years. Early stage geophysical estimations take account of the stable conditions of methane hydrates and geological conditions [37], with estimations varying from $3.1 \times 10^{15} \text{ m}^3$ to $7.6 \times 10^{18} \text{ m}^3$ at Standard Temperature and Pressure (STP) [38]. With the developments of seismic survey and information from the Ocean Drilling Program (ODP) and the Deep Sea Drilling Project (DSDP), scientists started to reconsider the estimation errors. Kery and co-workers [39] also stated that the uncertainties of estimations are to some extent due to the limitations of the

seismic and electromagnetic logging techniques. It was estimated by the U.S. Geological Survey (USGS) [40] that the recoverable methane hydrate might only be 10% of the total amount of methane hydrates deposited around the world. Moreover, easily accessible methane hydrate reservoirs, which are located in permafrost and shallow seas, contain less condensed methane hydrates, which means methane hydrates appear along with sand or clay. Despite these issues regarding the recovery of methane hydrates, the total amount of methane hydrates is still enormous. Recent estimations of the methane hydrate inventory are consistently in the order of 10^{16} m^3 at STP, which surpasses the combined energy content of other conventional fossil fuels put together [41].

The locations of methane hydrate reservoirs were firstly detected by seismic surveys. They are widely distributed in the polar regions, continental shallows and deep seas [36]. The reflection data from deep-sea continental margins can be used to infer the locations of methane hydrate reservoirs. Normally, the survey is carried out from the seabed to several hundred meters beneath [42]. “Bottom-Simulating Reflectors” (BSRs) are regarded as a reliable seismic indicator of the presence of methane hydrate reservoirs. BSRs have no direct link with the layers of sedimentary deposition but are related to sudden physical property changes, which include temperature, pressure or both. These special intrinsic characteristics promote seismic surveys along with BSRs to be the ideal candidates for the initial detection of methane hydrate reservoirs [43].

Apart from seismic data, a range of drilling programs, initiated by different governments, provide more accurate information of the global methane hydrate inventory. Figure 2.5 shows the locations of the predicted and recovered reservoirs of natural gas hydrates.

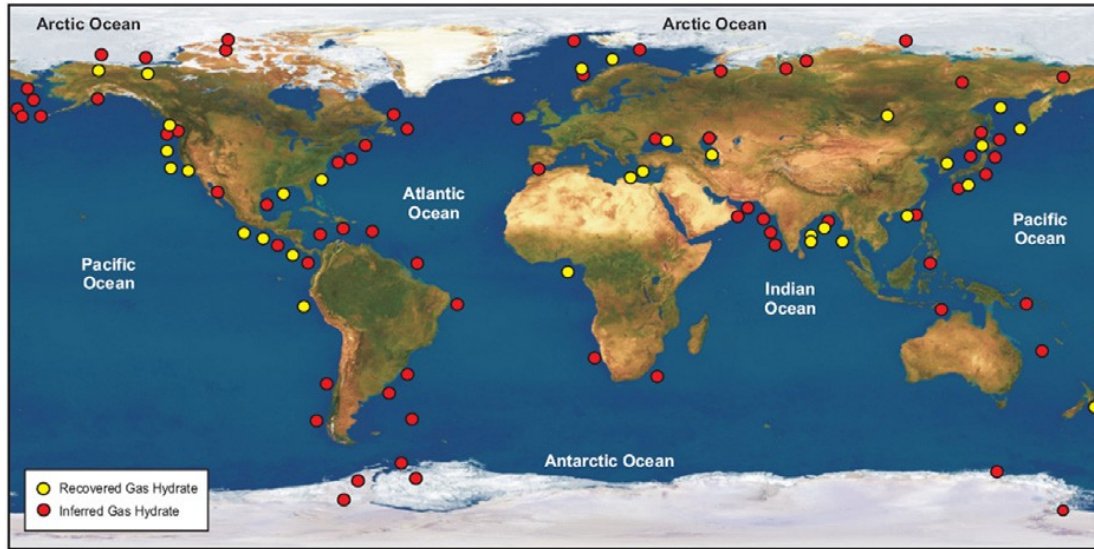


Figure 2.5 A global inventory of predicted and recovered natural gas hydrates. ●, Recovered reservoirs; ●, Predicted reservoirs. “ Reproduced from Krey et al. [39], Figure courtesy of the U.S. Geological Survey.”

This map takes account of the seismic and drilling program conducted by the USGS until 1999 [44], a review from Kvenvolden and Rogers [45] and a Canadian government report [46]. With the updated information, Figure 2.5 is a good interpretation of the state-of-the-art methane hydrate inventory distributions. In conclusion, the worldwide distribution of natural gas hydrates and their large volumes have the potential to supply a significant part of the energy demand for the future.

2.3.2 Potential Hazards to the Environment

Methane, as the main component of natural gas hydrates, belongs to the family of Greenhouse Gases (GHGs). The greenhouse effect of methane is much stronger than that of carbon dioxide (CO_2). The global warming potential index (GWP) of methane is 3.7 times as strong as that of CO_2 on a molar basis and 20 times on a weight basis [47]. Therefore, releasing large quantities of methane gas into the atmosphere results in serious climate effects [48]. It was estimated that the amount of methane gas trapped inside naturally occurring methane hydrates is 1800 times more than the amount of atmosphere methane gas [49].

The stability of methane hydrate reservoirs is governed by a few factors, including temperature, pressure, and types of reservoirs [44]. If global warming keeps its pace, some

methane hydrate reservoirs may exit the stable region and release methane gas to the atmosphere. Methane gas has strong short-term effects on the global temperature within 20 years [47]. Therefore, releasing methane from methane hydrate reservoirs could possibly initiate a vicious circle of temperature escalation through a positive feedback mechanism.

2.3.3 Depositional Conditions of Natural Gas Hydrates

In order to form methane hydrates, appropriate temperature and pressure conditions must prevail. In principle, the temperature and the pressure have to be suitable to stabilise the clathrate structure. In general, low temperatures are preferred (ca. 273 K) and pressures have to be higher than 3 MPa. Low temperatures can be found naturally either on the continental shelf and in Polar Regions where the surface temperature is low or on offshore continental slopes where sea water is cold at the seabed. Moreover, due the earth/ocean thermal gradient, it has been estimated that methane hydrates could only exist at a range 300 meters to 2000 meters below the sea floor [44] (see Figure 2.6).

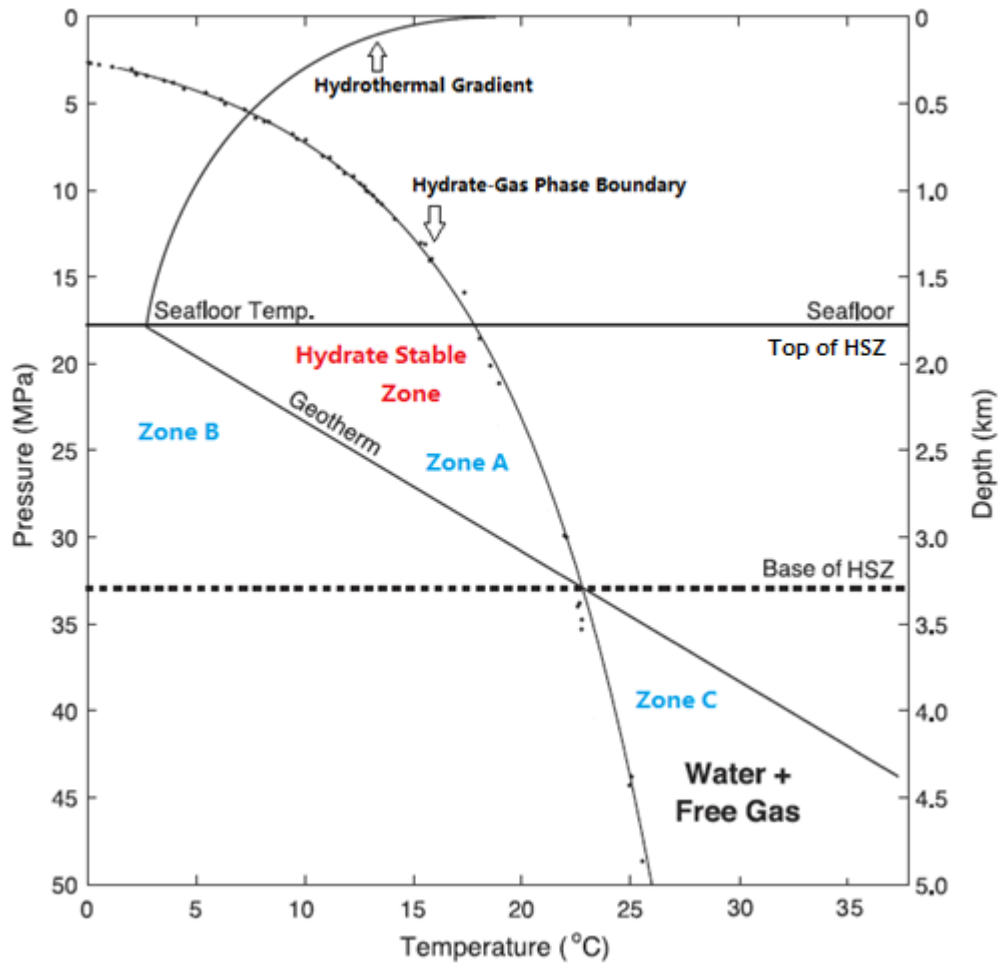


Figure 2.6 Methane hydrate stable zones in the deep sea area. “Reprinted from Archer et al. [50], Copyright (2004), with permission from Elsevier.” (HSZ, Hydrate Stable Zone; Stable hydrates exist in Zone A; hydrates are unstable in Zone B and Zone C)

Figure 2.6 illustrates a typical submarine hydrate stability zone. The actual temperature and pressure may vary depending on the reservoir conditions. There are five important lines that divide the hydrate stability zone into different sections.

- i) Methane hydrate phase boundary. Hydrates are only stable on the left side of the phase boundary.
- ii) Top of hydrate stable zone (HSZ) and bottom of hydrate stable zone. The HSZ marks the proper pressure and temperature conditions of hydrates and gas hydrates are only stable within this area. HSZ is typically identified by the seismic bottom-simulating reflectors. The top of HSZ is merged with the sea floor in this

case; it may differ from sea floor under different sea floor conditions depending on the actual temperatures and pressures.

- iii) Hydrothermal gradient line and geothermal gradient line: The thermal gradient lines mark the temperature conditions in the subsea area and below the sea floor, which determines the depth and thickness of the HSZ.

There are three important areas that are defined by those five lines, which are labelled as Zone A, Zone B and Zone C. Stable hydrates exist in Zone A, where temperature and pressure conditions are suitable for methane hydrates. In Zone B and Zone C, the temperature is higher than the equilibrium temperature of methane hydrates. Hence, only methane gas and water are found in this area, which explains the occurrence of free gas below some of the hydrate reservoirs. Figure 2.7 illustrates the depositional conditions that are confirmed by drilling programs from USGS.

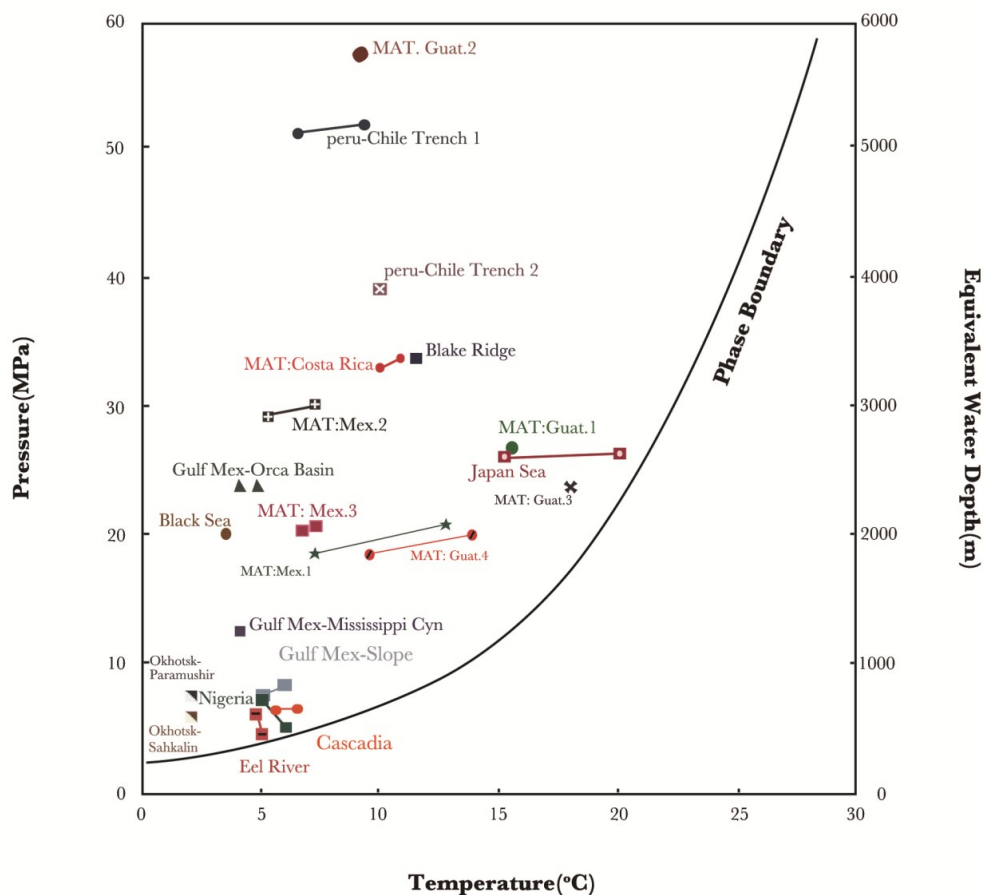


Figure 2.7 Recovered reservoir pressure and temperature conditions of gas hydrates. “Reproduced from Booth et al. [51], Figure courtesy of the U.S. Geological Survey.”

2.3.4 Production Methods of Natural Gas Hydrates

Technological advances have unlocked natural gas resources that were previously unrecoverable, such as deep-water reservoirs (depths > 300 m) and unconventional resources (e.g., shale gas). The next resource positioned to be delivered is gas hydrates [6]. Several production methods have been proposed to exploit methane hydrates during the recent decades. So far, none of them is validated to be the economical route for commercial productions. Figure 2.8 shows three potential production routes for methane hydrates.

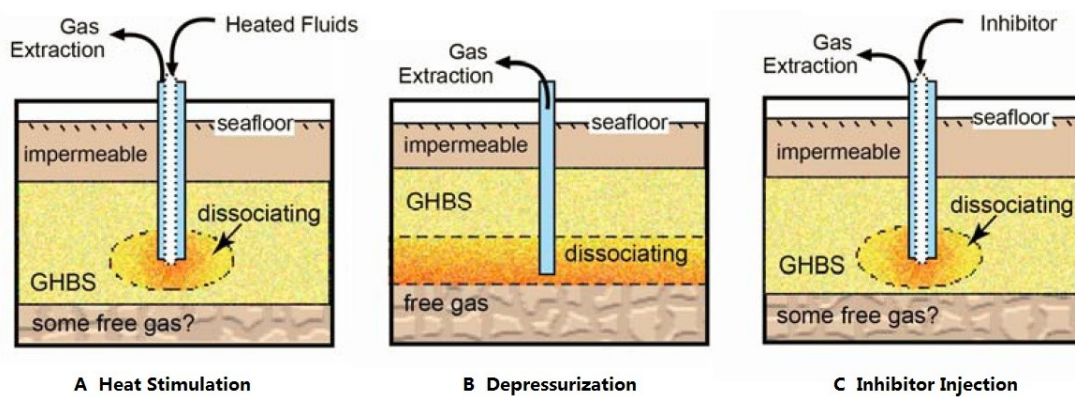


Figure 2.8 Three possible exploration methods of methane hydrates. “Reproduced from Ruppel [13], Figure courtesy of the U.S. Geological Survey.”

An impermeable layer normally exists between the seafloor and gas hydrate-bearing sediments (GHBS). Below the GHBS, depositional sediment, usually along with free gas, can be detected [13].

- A. Heat Stimulation Method involves directly supplying heat into the reservoir, leading to dissociation of the clathrate structure and releasing methane gas and free water. As proposed by different researchers, the heat source could be steam or hot brine [52, 53], downhole combustion [54, 55] and other heating sources like microwave heating [56]. This scenario involves supplying a large amount of energy to compensate the heat of dissociation of methane hydrates. Therefore, the operating cost is considerably high.
- B. Depressurisation Method is possible to be commissioned with the conventional drilling and well systems. By reducing the pressure inside the reservoir, methane hydrates become unstable. Similar to the heat stimulation method, the depressurisation method results in

the decomposition of methane hydrates and inevitably reduces the temperature inside the reservoir due to the heat of dissociation. Low temperatures could lead to secondary hydrate formation, which might result in a reduction of the production rate [13].

C. Inhibitor Injection Method utilises a different mechanism compared to the aforementioned methods. While heat stimulation and depressurisation methods move the reservoir conditions out of the phase boundary, inhibitors alter the phase equilibrium of methane hydrates. As noted previously, methane hydrate inhibitors have been used in the oil and gas industry for many years. Methanol and mono-ethylene glycol (MEG) are commonly used to prevent methane hydrates during transportation. However, the cost of the chemicals can lead to significant operating costs during productions [57].

The proposed production methods require large energy input or high operating costs: a combination of two or three methods may generate a possible pathway to a viable production method in the future. In addition, the production of gas hydrates from the aforementioned methods may cause the destabilisation of gas hydrates in the reservoir, increasing the risk of geological hazards like marine landslide and tsunamis [44]. Instead, carbon dioxide hydrates are thermodynamically more stable than methane hydrates, suggesting an alternative way to recover methane from methane hydrates while capturing carbon dioxide and maintaining the geological stability of the reservoir. A detailed review of $\text{CH}_4\text{-CO}_2$ exchange studies is given in Chapter 6.

2.3.5 Pilot Production of Natural Gas Hydrates

The abundance of the clathrate makes the research on methane hydrates a long-term investigation for the governments and for oil/gas companies [20].

USA, Japan, Canada, China, India, and Korea initiated national projects more than a decade ago. More recently, the research on methane hydrates has moved from the laboratory scale to field pilot productions. The first pilot production was carried out in a permafrost NGH reservoir in Mallik, Canada. In 2002, the thermal stimulation method was tested. Hot water was circulated through the natural gas hydrate reservoir, and 470 m^3 methane gas was

produced in five days ($94 \text{ m}^3/\text{day}$). In 2008, a second pilot production, joined by Canada and Japan, was conducted in Mallik, where the depressurisation method was used. Approximately $13,000 \text{ m}^3$ methane gas was produced in six days ($2166 \text{ m}^3/\text{day}$) [58].

In February of 2012, another pilot production using the gas exchange method was carried out in Alaska, USA. About 5900 m^3 (at STP) of mixed CO_2 and N_2 , with the molar ratio of 23% to 77%, was injected into the methane hydrate reservoir. The injection took 13 days. Three days after the injection, the well was reopened, and the pressure was reduced. The production lasted for 30 days, leading to 27756 m^3 of mixed gas, among which 86.7% (volume ratio) was methane ($925 \text{ m}^3/\text{day}$) [59, 60].

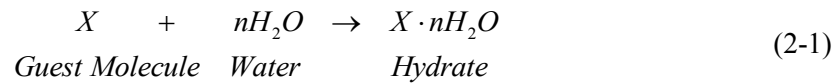
Japan announced a successful pilot production by depressurisation method on 19th March 2013 in the Eastern Nankai Sea. During the production of 6 days, approximately $120,000 \text{ m}^3$ methane gas was obtained ($20,000 \text{ m}^3/\text{day}$), during which a significant amount of free water was produced and pumped back into the ground. Similar observations were also made during the pilot production at Mallik, Canada in 2008. The production was terminated due to an equipment failure caused by sands during the production [61].

The most recent successful extraction of natural gas hydrates was announced by the China Geological Survey in 2017. The pilot production was commenced in the South China Sea and the depressurisation method was used. A total of $120,000 \text{ m}^3$ methane gas (at STP) was extracted in eight days ($15,000 \text{ m}^3/\text{day}$), with a peak production of $35,000 \text{ m}^3/\text{day}$. The purity of methane in the extracted gas was 99.5% [62].

The prospects for extracting methane from natural gas hydrates has been greatly improved through these pilot-scale productions. The next challenge stems from the economic side. Relatively high gas production rates are necessary to make the expensive deep-water extraction commercially feasible. There remain technological challenges to be tackled during the production, including sand accumulations, secondary formations of hydrates, and stability of the geological settings [6].

2.4 Formation of Gas Hydrates in Laboratories

There are two conventional hypotheses on the mechanism of hydrate formation. The simplest interpretation would be whether the gas molecules participate in the first stage of forming gas hydrates. One hypothesis states that water molecules are linked by hydrogen bonds to form the lattices into which guest molecules enter at a later stage. The other hypothesis says that dissolved methane gas participates in the initial formation of the lattice. Once the lattices are built up, more gas molecules are absorbed into the solid phase [16]. The formation process which involves water and guest molecules is given in Eq. 2-1.



Here, n is the molar water to guest molecule ratio. In an ideal case when methane molecules occupy all cavities that are formed by water in a Type I lattice, n is 5.75 [63]. For a binary mixture of methane and water, the exothermic hydrate formation releases heat and normally occurs at the liquid-gas interface where supersaturation exists. The formation rate of gas hydrates is determined by several factors including temperature, pressure, heat and mass transfer. When suitable temperature and pressure conditions are provided, hydrates can be readily formed after an initial induction time [64]. In the laboratory environment, a real challenge is to achieve high conversion of gas hydrates.

Most Researchers adopted Stern's method to form methane hydrates in laboratories [65]. Granular ice (180 μm to 250 μm in diameter) was used as the starting material, which provided large surface areas to contact with methane gas. The temperature and pressure conditions were selected to be several degrees Celsius below the equilibrium conditions, while the temperature was still below the ice point. It normally took about 8 hours to several days to achieve a conversion of 87% to 98% without any agitation (97% [65], 91% [66], 91% in porous conditions [67], and 87% [68]).

When a binary mixture of water and gas (e.g., methane) is used as the starting material, an agitated system can enhance the mass transfer and the heat transfer. A continuous flow stirred tank reactor (CSTR), or a stirred bath reactor is normally used for the continuous or batch production of gas hydrates [69]. It was reported that the presence of surfactant could enhance the growth rate and reduce the induction time during the formation of methane hydrates [70]. Extra caution should be taken since the obtained hydrate sample with surfactants may also have a substantial effect on the following analysis.

Japan also built a pilot plant in efforts to produce methane hydrates continuously. A CSTR was used at a temperature of 263 K and a pressure of 10 MPa. Methane hydrates were formed at the interface of methane and water and removed by a circulating pump. The solid phase was sieved and packed in a liquid nitrogen environment. The packed methane hydrate pellets were 12 mm in diameter and were proposed as a transporting media for methane gas. The capacity of the Japanese plant is 5000 kg/day [69].

The rate of mass transfer is normally faster in liquid-gas systems than for solid-gas systems. However, without sufficient agitations in a liquid-gas system, accumulated hydrates at the liquid-gas interface may act as a strong mass transfer barrier which inhibits the further formation of methane hydrates. An oscillating temperature method [71] is normally used in systems without any agitations. A relative large driving force (i.e., 243 K at 10 MPa) was provided to initiate the formation process. Hydrates were normally formed along with ice. The system temperature was then set to oscillate between a low-temperature set point (i.e., 243 K) and a high temperature set point above the ice point (i.e., 278 K). The high temperature set point was always lower than the equilibrium temperature of gas hydrates. In each oscillating cycle, a fraction of melted ice would be converted into hydrates. For a small amount of initial sample (less than 100 mg), a relatively high conversion (> 80 %) can be expected after a number of cycles (ca. 20).

Chapter 3

Formation Kinetics of Methane Hydrates

3.1 Overview

It is essential to understand fundamental properties of gas hydrates, due to their great energy potential and impacts on flow assurance issues. The most intriguing challenge concerns how hydrates form and dissociate with time. Time-dependent phenomena are considerably more challenging than the time independent phenomena of thermodynamics and structure. Time-dependent measurements and models are expected to be at least one order of magnitude less accurate than those from time-independent thermodynamic properties [16]. One of the key properties is the formation kinetic of gas hydrates; it is critical for producing suitable samples in laboratories and providing key parameters for flow assurance simulators.

The objective of this part of the work is to investigate the dependence of hydrate formation kinetics on accessible gas-water surface area, temperature, and pressure and to investigate discrepancies in some of the literature concerning ‘reactor dependent formation rates [72-74]’. In this work, a piece of high-pressure, low-temperature apparatus was modified to conduct hydrate formation kinetic studies in a temperature range 276.5 to 283.5 K and a pressure range 5 to 10.5 MPa with a special focus on the impact of the interfacial surface area on which the hydrate formation occurs. This was to be achieved by studying three different forms of water pre-cursor to enable the methane-water interfacial area available for gas mass transfer to be varied over a very wide range. The first system was a conventional stirred liquid water system where the interfacial area could be varied by controlling the curvature of the liquid surface via the stirrer speed, remaining within the laminar regime to avoid gas entrainment. The second system was ‘Dry Water’, in which water at high mass fraction (94 wt%) was dispersed as small droplets (size $\sim 190\ \mu\text{m}$) within a dry Pickering emulsion stabilised by silica nanoparticles. This Dry Water system gave a much higher available

interfacial area compared to the stirred bulk liquid system. Finally a micronised ice slurry (particle size $\sim 7 \mu\text{m}$) was used, which also gave a much higher available interfacial area for mass transfer but would also have much lower mass transfer within the solid ice phase compared to the two liquid water systems.

3.2 Literature Review

The formation of methane hydrates consists of three steps, namely an induction period, hydrate nucleation, and hydrate growth. The induction time is defined as the time elapsed until hydrates can be detected macroscopically. During the induction period, the temperature and the pressure of the system are set to be in the hydrate stable region, but gas hydrates are not readily formed because of their metastability [16]. In laboratory environments, nucleation of hydrates is treated as a heterogeneous process. Due to the stochastic nature of heterogeneous nucleation, the induction time has large variations ranging from a few seconds to 167 minutes or greater even though the temperature and pressure conditions are favourable for the formation of gas hydrates. Studies indicate that with a large thermal driving force, the induction time is less stochastic, and has narrower distribution ranges [75, 76]. Hydrate nucleation is the process when water and gas (hydrocarbon) molecules form clusters (hydrate nuclei) and grow to critical sizes for continuous hydrate growth [77]. Hydrate growth occurs after the nucleation step when significant amounts of methane gas are densely packed into the clathrate structure. A number of studies confirmed that nucleation and subsequent growth of hydrates typically occur at the water-gas interface where supersaturation of gas molecules exists [64, 78-80]. Past studies have shown that the displacement from equilibrium conditions controls the formation rate of gas hydrates, which increases with decreasing temperatures and is promoted by elevated pressures. The combined pressure and temperature effect is called 'driving force' [81]. Driving force has been expressed in terms of different variables by different researchers, including fugacity [82-84], concentration [85], temperature difference [64, 86], Gibbs free energy [16], and chemical potentials [87, 88]. Arjmandi [86] suggested that temperature differences could solely represent the driving force for single guest

component hydrates, whereas Sloan and Koh [16] proposed using a comprehensive driving force that includes both pressure and temperature effects (i.e., Gibbs free energy).

In 1983, Vysniauskas and Bishnoi [64] conducted the first systematic study on hydrate formation of methane and water in a stirred reactor in a temperature range 274.2 to 281.0 K over a pressure range 3 to 10 MPa. The experiments were performed at constant pressure and constant temperatures with a stirrer speed of 500 rpm. The authors concluded that the formation rates depended on the degree of subcooling, temperature, pressure, and the gas-liquid interfacial area. The interfacial area was calculated by the shape of the vortex at ambient pressure, which might be different at high-pressure conditions due to different contact angles and interfacial energies at elevated pressures. An Arrhenius-type semi-empirical model was proposed to correlate the experimental data, and the activation energy for hydrate growth was estimated to be 106.24 kJ/mol. Freer and co-workers [78] also used an Arrhenius-type correlation to calculate the activation energy for hydrate growth based on methane hydrate film growth rate. The activation energy was calculated to be 171 kJ/mol.

In 1987, Englezos and co-workers [83, 84] proposed that the reaction surface area of hydrate formation should be the surface area of solid hydrate particles in the system. The formation rate of methane and ethane hydrates was measured isothermally and isobarically during the initial growth stage within 85 minutes at temperatures from 274 to 282K and pressures from 0.636 to 8.903 MPa. The authors also pointed out that nucleation was normally observed at the liquid-gas interface but also in the bulk liquid phase. They did not take into account that the hydrate crystals might be transported from the liquid-gas interface by agitations. With a population density function that considered both primary and secondary nucleation, a fugacity-based model was proposed to correlate the experimental data. They reported a reaction rate constant of the order of 10^{-6} mol/(m²·s·MPa). It was also found that gas mixtures, which altered the fugacity of each component, had a significant effect on formation rates of hydrates.

Malegaonkar and co-workers [89] studied the kinetics of methane and carbon dioxide hydrate formation using a modified version of the model of Englezos and obtained a reaction rate

constant of the order of 10^{-5} mol/(m²·s·MPa) and 10^{-4} mol/(m²·s·MPa) for CH₄ hydrates and CO₂ hydrates respectively. Chun and Lee [90] also used Englezos's model to correlate the results of carbon dioxide hydrate formation kinetics. They reported the reaction rate constant for CO₂ hydrates were two orders of magnitude smaller than that from Malegaonkar. Clarke and Bishnoi [91] measured the particle size distribution of solid CO₂ hydrates during formation and used Englezos's model. The reaction rate constant was in the order of 10^{-3} mol/(m²·s·MPa).

Herri and co-workers [92, 93] commenced hydrate formation studies with an optical sensor for measuring the *in-situ* particle size distribution of methane hydrate particles at 274.15 K and pressures from 3.5 to 5.5 MPa. It was observed that the mean particle size increased at a low stirring rate (250 rpm), remained constant at a stirring speed of 400 rpm, and decreased at a high stirring speed of 600 rpm. The number of crystals and the gas consumption rate increased with the increase of stirring speeds. The authors proposed a mechanistic model which takes into account two separated regions. At the interface, primary nucleation occurred under supersaturation, while in the bulk liquid, secondary nucleation and crystal growth took place and the secondary nucleation and growth rate depended on the supersaturation of the aqueous phase. The authors also concluded that primary nucleation at the interface was sufficient to describe the early stage of hydrate formation. The methods used to determine the surface area of the liquid-gas interface, which was crucial to quantify the primary formation rate, was not mentioned.

Skovborg and Rasmussen [85] revisited the data of Englezos and co-workers and proposed that mass transfer at gas-liquid interface controlled the formation rate and thus it was independent of the total particle surface area. A mass transfer limited model based on fugacity was proposed to describe the formation rate of methane hydrates. The authors also noticed that after 40 minutes of linear molar consumption of methane gas, the formation rate of methane and ethane hydrates decreased, which might be attributed to a reduction in the interfacial area due to hydrate accumulations at the interface. Mohebbi and co-worker [80] also conducted two types of experiments under isochoric and isobaric conditions in a stirred

batch reactor of 0.44 L. The results showed that isochoric and isobaric conditions led to similar molar consumption rates of methane during hydrate formation. Since the particle size distribution would be altered by the driving force, the results suggested that the gas consumption rate was independent of the total hydrate particle surface area. They also observed that with a 4 cm magnetic stirring bar, a rotating speed of 300 rpm was not sufficient to maintain the gas-liquid interface free of hydrate blockages. At 400 rpm, gas bubbles were observed. The interfacial area was estimated by a digital camera through a double walled window.

Meindinyo and Svartaas [74] commenced the formation of gas hydrate studies in two batch stirred autoclave reactors with volumes of 0.14 L and 0.38 L. It was found that supersaturation, stirring rate, and reactor size all had impacts on the formation rate of hydrates. The effects of reactor size were likely attributed to the different hydrodynamic conditions. It was also found that temperature in the reactor rose by up to 5 K during the hydrate formation process, suggesting a heat transfer-limited formation process in the reactors. A temperature increase was also observed by Arai and co-workers [94] when the formation rate of methane hydrates was studied in a 1.2 Litres stirred reactor. It was also found that low temperatures and high pressures promoted the hydrate formation. Happel and co-workers [95] measured the formation rate of methane and nitrogen hydrates with a special focus on separating nitrogen from methane in a continuous stirred tank reactor of 1 L. The measured formation rates of methane hydrates were significantly higher than those from Vysniauskas and Bishnoi's measurements. The amplified reaction rates were likely attributed to the higher stirring rate employed (up to 2250 rpm).

The formation rate studies have also extended to other systems including propane hydrates [96], methyl bromide hydrates [97], structure H hydrates [25, 98], natural gas hydrates [99] and gas hydrates with additives (i.e., promoters and inhibitors) [79, 100, 101]. However, the importance of gas-liquid interfacial area was not addressed in those studies, and the formation rates were customarily described as 'reactor dependent'. It was therefore decided to investigate the role of gas-water interfacial area on the formation kinetics for a variety of

different forms of the water precursor in an attempt to characterise the mass transfer in a way that would be transferable to different reactor and gas-water contacting configurations.

3.3 Materials

Research grade methane was supplied by BOC with a specific minimum mole fraction of 0.99995. Deionised water with an electrical resistivity higher than 18 M Ω ·cm at 298 K was obtained from a piece of reverse-osmosis apparatus (Millipore, Direct-Q3). Silanised silica powders (Aerosil, R812S) were purchased from Evonik UK Ltd. Toluene, acetone, and propan-2-ol used in this work for cleaning purposes (Sigma-Aldrich, UK) were of purity 95% or higher.

3.4 Apparatus

A high-pressure and high-temperature reactor (Thar Process, SPM20) was modified for studying the formation kinetics of methane hydrates. The apparatus, shown schematically in Figure Figure 3.1, consisted of a pressure reservoir with a gas regulator, a liquid nitrogen (LN₂) assisted cooling system, a variable volume cell, and a magnetically coupled high-pressure motor. Wetted metallic parts were made from 316 and 304 stainless steel.

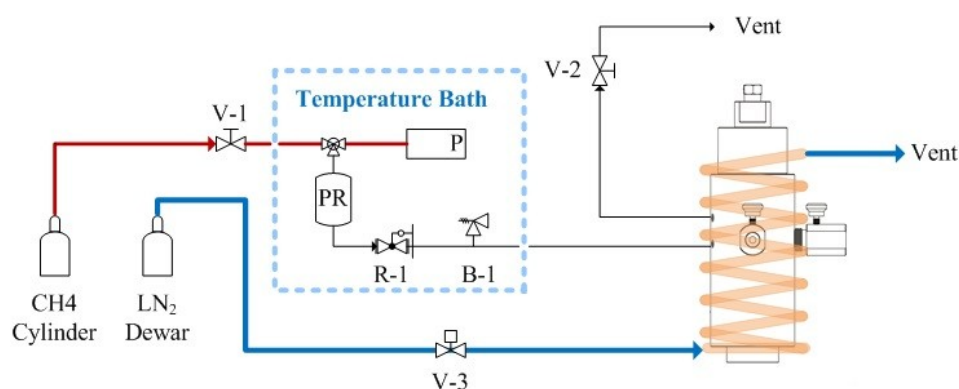


Figure 3.1 Schematic diagram of the formation kinetic apparatus: V-1 and V-2, on-off valves; V-3, solenoid LN₂ valve; P, pressure sensor; PR, pressure reservoir; R-1, gas regulator; B-1, safety head with bursting disc; — 1/16" high-pressure tubing, — 1/8" high-pressure tubing — 1/4" low-pressure tubing.

The core of the apparatus was a variable volume autoclave reactor which was originally designed to work in a temperature range 298 to 423 K and pressures up to 41.4 MPa with the motor attached. The internal diameter of the cell was 20 mm. The bottom of the cell was fitted

with a movable piston allowing the internal height of the cell to range from 16 to 29 mm, leading to a volume from 0.5 to 15.5 mL. Four connection ports (Valco 1/16" and 1/8" connections) facilitated the connections of fluids (Figure 3.2 A and C) and two temperature probes (Figure 3.2 B and D). The temperature probes were sealed by PEEK ferrules (IDEX, UPLT-100) to minimise thermal contact of the cell with the temperature probes. Two sapphire windows which were sealed by PTFE (Teflon) O-rings (I.D 1/4" C.S. 1/16", Swagelok, T-0-OR-010) accommodated a camera and a light source. The PTFE gasket was required to be further tightened up at low temperatures due to the different coefficients of thermal expansion of 316 steel and PTFE. Miniature Xenon bulbs (Maplin, LM2A001) were used and found to be superior to halogen and LED bulbs regarding light intensities for visual observation. A 15 Ω potentiometer (RS Components, 10RJH4) was connected in series with the Xenon bulb to allow incremental adjustments of the light intensity.

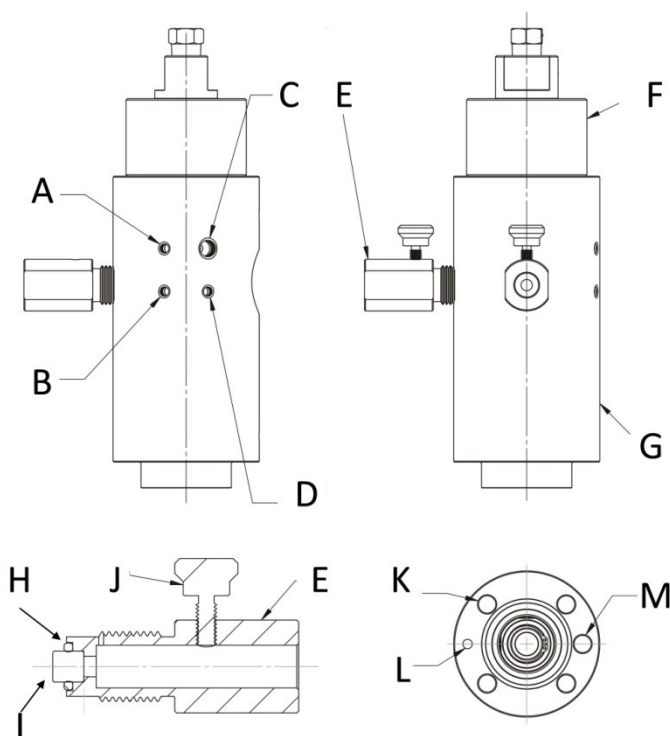


Figure 3.2 Engineering drawing of the high-pressure reactor: (A) fluid inlet; (B) Temperature control probe; (C) Temperature measuring probe; (D) Fluid outlet; (E) Camera adapter (F) Magnetic coupled motor or motor plug; (G) Cell body; (H) Teflon seal; (I) Sapphire window; (J) Thumb screw; (K) Electric cartridge heater 4 places; (L) Ground screw; (M) Additional temperature probe port. "Image reproduced from the user manual of Thar Process SPM20 with the permission of Waters Limited."

High temperatures were achieved by using four cartridge heaters (120 V, 50 W) fitted in vertical holes (Figure 3.2 K) in the cell body. A copper coil (4mm O.D., RS Components, 846503) spiralled around the high-pressure cell (see Figure 3.3 ii), and the thermal contact was improved by means of a silicon based thermal paste (RS Components, 7074736) with a thermal conductivity of $5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Liquid nitrogen (LN_2) was withdrawn from a pressurised liquid nitrogen Dewar vessel (Statebourne Cryogenics, Cryostor 60) and the flow was regulated by a solenoid on-off valve (Emerson, SCE263B206LT-230/50). A cascade temperature controller (Schneider Electric, Nanodac) regulated both the heating power and the flow rate of liquid nitrogen.

The controller was interfaced with a computer by an Ethernet cable, which allowed remote temperature set points to be made. A combination of a time proportional control for the on-off valve and a Pulsed Width Modulation (PWM) control for the heaters was chosen to provide a stable temperature output ($\pm 0.1 \text{ K}$). PID (Proportional integral and derivative) parameters were tuned separately for sub-ambient temperatures and elevated temperatures. The reactor was well insulated from the ambient conditions with three layers of silicon sponge (10 mm thick, Polymax, 3010145). It was also found that gas-liquid and gas-solid (i.e., ice and Dry Water) systems required different PID parameters to achieve the desired temperature stability ($\pm 0.1 \text{ K}$). The LN_2 transfer line was insulated by polyethylene foams (Climaflex, 1/4" I.D.), the length of which was kept to the minimal level to prevent the potential loss of liquid nitrogen during the transfer process. The pressure reservoir was immersed in a refrigerated temperature bath (Grant, TFX200-R5) at 289 K.

Agitation of the reactor was achieved by a magnetic coupled high-pressure motor (see Figure 3.3i A) and a customised axial impeller (see Figure 3.3 iii). The customised axial impeller was machined from PTFE (Industrial Plastics, Virgin grade) to provide strong circulation in the fluid phase and minimise gas entrainments. A second impeller could be attached on to the shaft for gas phase mixing. A pair of magnets was placed inside and outside the high-pressure reactor, and a DC brushed motor was connected to the external magnets. A pair of Rulon bearings were originally used for the internal magnet and found to be degrading under

high-pressure and high rotating speeds. A carbon-filled PEEK (Quadrant EPP UK Ltd, Ketron CA30) bearing was made and used as a replacement due to its high thermal conductivity and mechanical strength. The motor was powered by two linear DC power supplies (AIM-TTi, QL564P) connected in series and interfaced with the lab computer via GPIB cables. The speed of the motor was measured by a magneto-resistance sensor (Bernstein Safety, 6372261085, Figure 3.3 B) with a ± 10 V square wave output. A closed loop speed control was achieved by using an Agilent 34980A data acquisition unit to measure the speed of the motor linked to the Agilent VEE program to adjust the power output based on the *in-situ* speed. A VEE-based PI control program was found to be sufficient to control the speed up to 1400 rpm ± 10 rpm. A torque parameter of 590.19 N·mm·amp⁻¹ supplied by the motor manufacturer was used to convert the motor current into torque numbers.

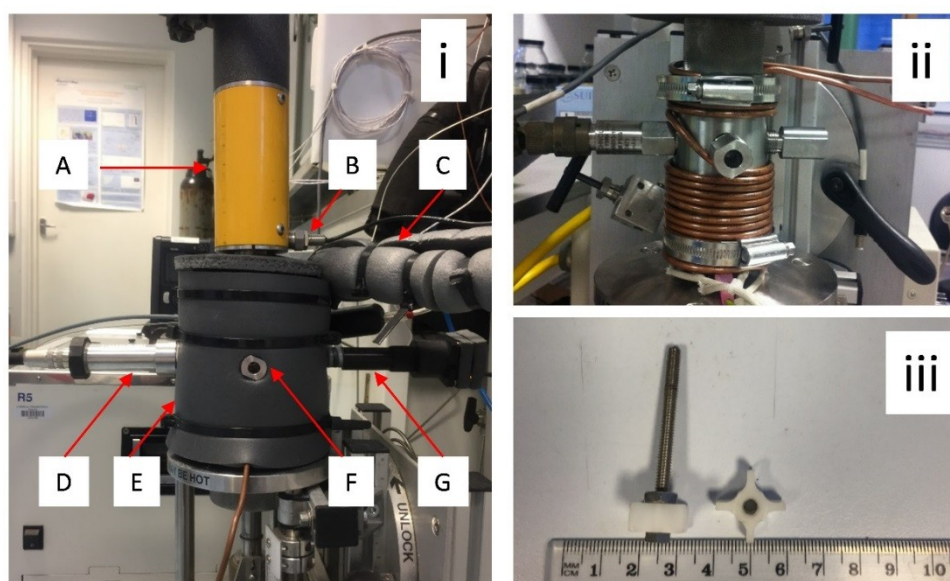


Figure 3.3 Pictures of the high-pressure autoclave reactor showing i) the main parts of the Thar reactor; ii) Arrangement of the copper cooling coil; iii) Axial impeller. A, Magnetic couple motor; B, Magneto-resistance sensor; C, Insulated LN₂ transfer line; D, Reactor pressure sensor; E, Insulation foam; F, Viewport for the light source; G, Camera.

The reservoir pressure was measured by a strain gauge pressure sensor (Omega Engineering, PX02C1-7.5KGI) with current outputs from 4 to 20 mA and a full-scale range of 51.71 MPa. Current output sensors are generally ideal for long distance signal transmissions and immune to electrical noise environments. No obvious differences were observed between current output sensors and voltage output sensors in the lab environment. The reactor pressure was

measured by a piezoresistive pressure sensor (Keller, PA-33X) with dual outputs (RS 485 and 0-10 VDC) and a full-scale range of 30 MPa. Four-wire resistance PT100 sensors (Omega Engineering, PR-11) were used to measurement room temperature, bath temperature, and reactor temperatures (two probes were used). One of the reactor temperature sensors was connected to the temperature controller, and the other temperature sensors were connected to the Agilent data acquisition unit fitted with a high-precision multimeter for four-wire resistance measurements.

A miniature bursting disc (Wehberg Safety GmbH, 101958) was connected to the high-pressure reactor with a nominal bursting pressure of 20 MPa. A cut-out current of 150 mA was set in the motor control program in Agilent VEE. Although the design of the motor allowed the motor to be stalled for a few hours, it was better to add an extra safety limit. The maximum heating power was limited to 10% of the total power (200 W), resulting in a maximum system temperature of 323 K. A low-temperature limit of 243 K was also set by the temperature controller. It was found that temperatures below 243 K led to excessive leakages of the system, which might be attributed to the glass transition of the polymer sealing gaskets (Waters, 700006715) in the system. A type T thermocouple (Omega Engineering, 5SRTC-TT) was used to monitor the temperature of the LN₂ solenoid valve. In case the LN₂ in the Dewar vessel depleted, the solenoid valve might be subject to continuous opening and over-heating. Should the temperature of the solenoid valve rise above 318 K, a safety cut-out of the temperature controller would be triggered.

3.5 Sensor and Reactor Calibration

Temperature readings from four 4-wire PT100 probes with nominal resistances of 100 Ω at 273.15 K were compared with a standard platinum resistance thermometer having an expanded uncertainty of 2 mK. By using a resistance constant of $0.00385 \text{ } \Omega \cdot \Omega^{-1} \cdot \text{K}^{-1}$, the uncertainty of temperature was estimated to be $\pm 0.2 \text{ K}$ over the experimental temperature range 253 to 293K.

The upstream pressure sensor with a full range of 51.71 MPa was calibrated by comparison with a quartz pressure sensor in a pneumatic calibration apparatus (Fluke-DHI, PPCH-G-70M). The expanded uncertainty of the Omega pressure transmitter was 58.3 kPa with a coverage factor $k = 2$ from the manufacturer's calibration. The uncertainty was reduced by conducting a calibration at pressures in a pressure range 1 to 13.8 MPa and allowing the linear calibration curve to have an intercept. Extrapolation of the calibration curve is not recommended. Since the pressure sensor always worked in pressure descending modes during the hydrate formation experiment, the calibration was performed from 13.8 MPa with a stepwise reduction in pressures to minimise the effects of hysteresis of the pressure readings. It was estimated that the expanded uncertainty of the pressure transducer after calibration was 12.3 kPa with a coverage factor $k = 2$. A calibration of the downstream pressure sensor's (Keller Model 33X) digital output (RS485 signal) was provided by the manufacturer. A numerical algorithm which takes into account non-linearities and temperature dependencies was implemented in a microprocessor in the pressure sensor. The expanded uncertainty of the RS 485 signal outputs over the full range of 30 MPa was estimated to be 13.6 kPa with a coverage factor $k = 2$.

A Magneto-resistive rotating speed sensor was calibrated at speeds in a range 150 to 3000 rpm by comparison with a stroboscope (RS Components UK, DT-2239A) with an accuracy of 1 rpm. It was observed that the rpm readings from the magneto-resistive sensor were within the accuracy of the stroboscope.

The volume of the reservoir was calibrated gravimetrically. The reservoir was evacuated with a vacuum pump (Vacuubrand, MZ2DNT) to 10 mPa. Degassed and deionised water was introduced into the reservoir at 0.2 MPa by a HPLC pump (Knauer, Smartline Pump 1000) at a flow rate of 1 ml/min. The mass of the added water was measured by an analytical balance with a resolution of 0.001 g. The density of water was obtained using the IAPWS formulation 1995 with an uncertainty in density of 0.001% at pressures up to 10 MPa [102]. The interfacial area of liquid-gas was estimated by agitating water in a transparent cylindrical container at ambient conditions. The surface area of the liquid-gas interface was calculated by

reconstructing 2D vortex images into 3D shapes in Solidworks 2016 software and estimated to be $11.5 \text{ cm}^3 \pm 0.2 \text{ cm}^3$ at 850 rpm.

3.6 Methods and Operating Procedure

Prior to the first use, the high-pressure reactor was cleaned thoroughly with toluene, propan-2-ol, and acetone in sequence for several times. The residual acetone was removed by overwriting the temperature set point to 343 K and keeping the temperature isothermally for 2 hours. Around 12 gram of deionised water was introduced into the reactor by a syringe and the sample mass was calculated by weighing the syringe before and after the injection on an analytical balance with a resolution of 0.001 g. The reactor was sequentially sealed, purged and pressurised with methane gas. The temperature was then set to the desired experimental conditions, and the pressure was set to 20 kPa below the equilibrium pressure of methane hydrates at this temperature. Pre-saturation of the water sample was achieved by agitating the water sample close to the equilibrium temperature-pressure condition at 850 rpm for 2 hours. After an equilibrium was established, suggested by stable temperature and pressure readings, the pressure set point was set to the desired experimental conditions by adjusting the pressure regulator. The rotating speed of the impeller was adjusted from the VEE user interface. The temperature of the refrigerated cooling bath, which contained the pressure reservoir and the gas regulator was set to 289 K throughout the experiment. The room temperature, bath temperature, reactor temperature, rotating speed, reservoir pressure, reactor pressure, and motor current were constantly recorded during the experiment.

Dry Water samples were prepared by aerating 50 g of deionised water and 3 g of silanised silica in a laboratory blender (Waring Model 7011S) at 22000 rpm for 90 seconds, resulting in homogenous white powders.

Micronised ice powders were synthesised by spraying deionised water into liquid nitrogen. Deionised water was delivered by a HPLC pump at a rate of 0.1 ml/min onto a Piezo ultrasonic atomiser (Farnell UK, M2313500). The atomiser was then activated by supplying a 143 kHz square wave signal ($\pm 10 \text{ V}$) from a wave generator (Agilent, 33220A). The droplets

with a narrow size distribution ($7.0\ \mu\text{m} \pm 0.5\ \mu\text{m}$ [103]) were then frozen in liquid nitrogen and particles larger than $50\ \mu\text{m}$ were removed by using a stainless steel sieve (IMPACT Laboratory Test Sieve, UK) in a liquid nitrogen environment. Scanning electron microscopy (SEM) images of the piezoelectric mesh were obtained by a benchtop SEM system (Hitachi, TM1000 SEM) with a 15 kV accelerating voltage and magnifications from 20 to 10000 times.

3.7 Results and Discussion

The formation rate of methane hydrates strongly depends on the pressure-temperature conditions and the degree of mixing affecting the interfacial area of water and methane during the formation process.

Other experimental factors that may affect the measurement of the formation rate include the dissolution of methane into the water and the temperature of the methane reservoir. The water sample was pre-saturated around the equilibrium pressure to minimise variations in the degree of further dissolution; an unsaturated water sample may increase the amount of methane consumed during the formation process and lead to an overestimation of the formation rate of methane hydrates. Due to the low solubility of methane and the slow dissolution kinetics, the dissolution of methane into the pre-saturated water sample had negligible effects on the pressure drop during hydrate formation measurements. The temperature of the reservoir was set to 289 K, limited by the temperature compensation range of the pressure sensor (289 K to 344 K), outside of which the output of the pressure sensor was expected to experience a significant drift. The temperature difference between the reservoir and the reactor had negligible effect on the temperature stability of the reactor due to the small thermal mass of the introduced methane gas compared with that of the reactor. The following sections investigate three main factors that affect the formation rate of methane hydrates from a $\text{CH}_4\text{-H}_2\text{O}$ binary mixture: the degree of mixing (rotational speed of the impeller), temperature, and pressure.

3.7.1 Formation of Methane Hydrates from the CH₄-H₂O Binary System

Under conditions that are favourable for hydrate formations, the amount of dissolved methane gas is orders of magnitude smaller than the amount of methane required to form the stoichiometric amount of methane hydrate. On the other hand, the high concentration gradient around the CH₄-H₂O interface provides a favourable condition for the primary nucleation of methane hydrates. It was observed that the nucleation of methane hydrates occurred at the water-gas interface (see Figure 3.4). Without sufficient agitation (i.e. with the rotating speed of the impeller smaller than 800 rpm), methane hydrates quickly formed a layer, which acted as a strong mass transfer barrier for further formations of methane hydrates at the interface. It is also worth noting that nucleation of methane hydrates from the liquid phase rather than at the liquid-gas interface was never observed in the early stages of hydrate formation (before 10 mol% of the water was consumed). Under higher rotating speed of the impeller (e.g., larger than 800 rpm), the hydrate layer was removed from the liquid gas interface and dispersed into the bulk by the water circulation, leading to continuous formation of methane hydrates at the CH₄-H₂O interface.

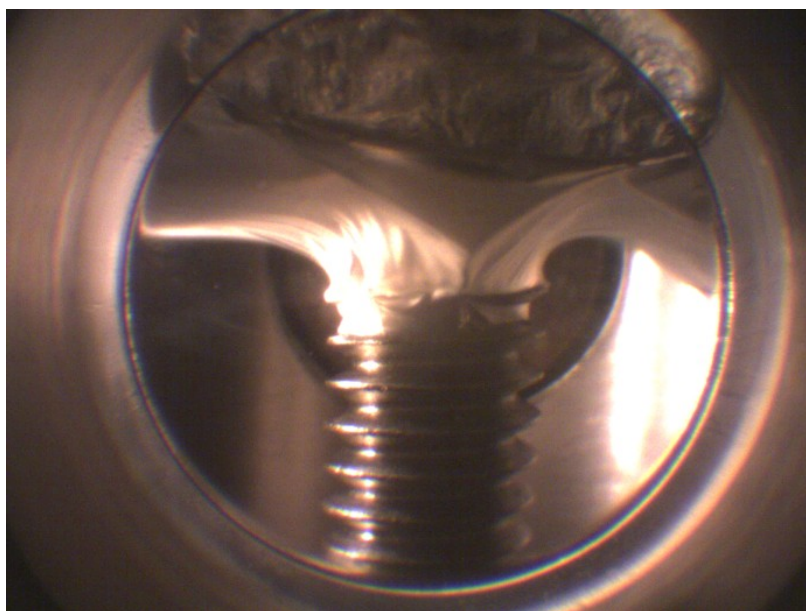


Figure 3.4 Methane hydrates formed at the interface of water and methane gas. The curvature of the hydrate surface was caused by agitation. The motor was stopped during the image capture.

Under sufficient agitation, the formation of the methane hydrates was measured by monitoring the pressure drop in the reservoir (see Figure 3.5 a). In a typical hydrate formation experiment, five distinct regimes (see Figure 3.5 I, II, III, IV, and V), which were: initial induction regime, linear formation regime, fast growth regime, mass transfer limited regime and end regime, were observed during the experiment.

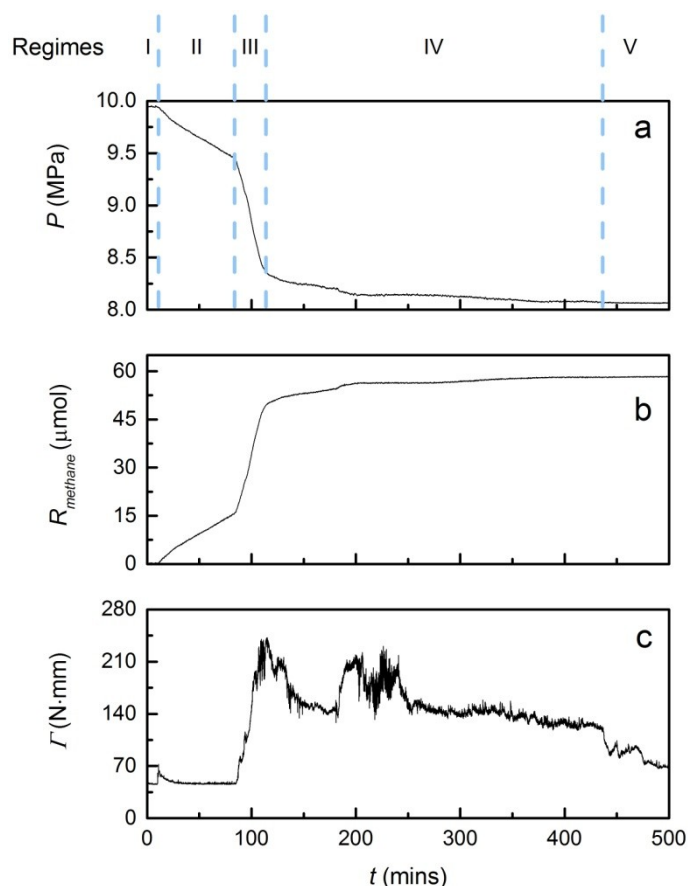


Figure 3.5 Formation of methane hydrates a) Pressure (P) drop in the reservoir b) Molar consumption rate (R_{methane}) of methane gas c) Torque (Γ) of the motor during hydrate formation with time (t). Regime I: Initial induction regime, Regime II: Linear formation regime, Regime III: Fast growth regime, Regime IV: Mass transfer limited regime.

The duration of the induction regime (Regime I) varied from minutes to a few hours, governed by the probability of the appearance of hydrate nuclei in the system. Under large driving forces ($\Delta T > 5$ K), the induction time was generally found to be shorter (less than 20 minutes). It was also observed that reusing all or part of the water sample from the melted hydrate samples for a new experiment significantly reduced the induction time. Such phenomena might be attributed to the ‘Memory Effect’ for gas hydrates, which is potentially

caused by residual hydrate structures or the dissolved gas remained in solution, leading to a reduction in the induction times [104].

Regime II was a linear formation regime in which hydrates were formed at the liquid-gas interface and quickly removed by the laminar regime circulations in the system (Reynolds number ~ 3300). The formation rate in regime II was governed by a several factors including the pressure driving force, the mass transfer at the interface, and the heat transfer (dissipating the heat from the exothermic formation of hydrates). The duration of the linear regime is governed by the rate of formation. Fast formation rates shortened the length of Regime II, during which the torque increased by 2%, indicating that the suspended hydrate particles increased the overall viscosity of the hydrate-water slurry. The slight increase of the viscosity had negligible effect on the mixing of the system. It was also worth noting that an intermediate regime might exist between regime II and regime III. In Figure 3.6, the gas consumption rate of methane hydrates was reduced after the initial formation stage of 320 minutes, which might be attributed to a hydrate layer formed at the gas-liquid interface. Due to the density differences of methane hydrates (0.94 g/cm^3 [16]) and water, hydrate particles tended to move to the interface. When large amounts of hydrate particles were accumulated, sometimes the agitation was not sufficient to renew the interface, leading to agglomerations and a partially reduced interfacial area (see Figure 3.6).

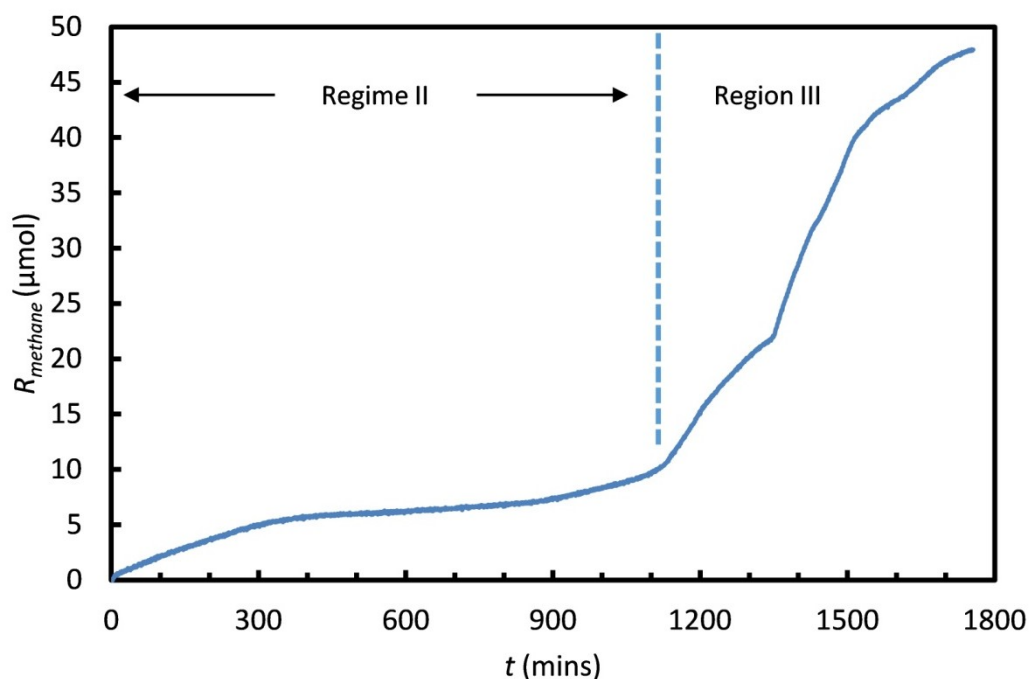


Figure 3.6 Amount of methane gas consumed (R_{methane}) with time (t) at 7 MPa and 276.5 K showing a reduced formation rate of methane hydrate (after ~ 400 min) after the initial Regime II linear formation regime, giving a reduced, steady formation region before entering Regime III, the fast formation regime.

In regime III, a large amount of hydrate particles were accumulated, leading to bulk nucleation of methane hydrates and a notable increase in the formation rate. A significant increase of the motor's torque was observed, suggesting that a large amount of hydrates emerged in the system and agglomeration might occur, leading to a large increase in the slurry viscosity. The formation rate in regime III was 5 to 10 times faster than that in regime II. However, the formation rate in regime III was not reproducible since the growth rate was not now depending on the interfacial area of the water-gas interface but relying on the number of hydrate particles and the available surface area of the solids (methane hydrate particles).

When the majority of the water molecules had been consumed, the hydrate formation transferred into a mass transfer limited regime (Regime IV). The formation rate decreased dramatically and approached zero over an extended period. In Regime IV, it is possible that residual water was trapped between hydrate crystals and became 'pore water'. Further growth relied on a mass transfer limited process of CH_4 molecules penetrating through the hydrate layer. As the hydrate layer grew further, the mass transfer barrier became significant, leading to a further reduction of the formation rate. It was also observed that the torque in the system

was declining in Regime IV and V. The descending trend might be attributed to the agglomeration of hydrates onto the shaft, leading to a cylindrical hydrate block (see Figure 3.7), which was rotating with the shaft.



Figure 3.7 Cylindrical block of methane hydrates formed by agitating water in a methane atmosphere.

In the following sections, only the linear formation rates in regime II were considered, where the formation rate was controlled by mass transfer across the controlled shape/area gas-water interface. The molar consumption rate of methane gas was calculated by using the volume of the reservoir, pressure drops of the reservoir, and molar densities of methane from the equation of state developed by Setzmann and Wagner with uncertainties in density of 0.03% under the experimental conditions [105]. Linear regressions were performed by Origin 9.0 software with a minimal Pearson correlation coefficient of 0.98.

3.7.2 Impact of Rotating Speed on the Formation Rate of Methane Hydrates

At fixed temperature and pressure conditions, the apparent formation rate in regime II (measured by the pressure drop in the reservoir) of methane hydrates is dependent on the available interfacial surface. When the fluid (i.e., water) was in different flow regimes (i.e., laminar regime, transition regime, and turbulent regime), the interfacial area was significantly altered, and the formation rate of methane hydrates changed accordingly (see Figure 3.8).

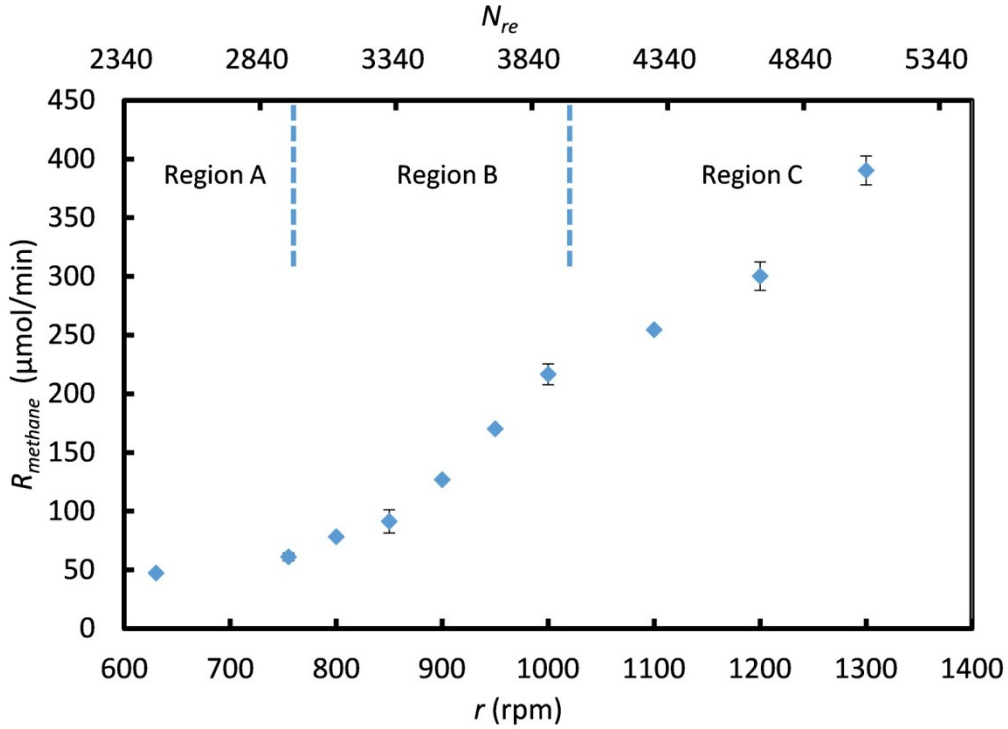


Figure 3.8 Apparent initial formation rate of methane hydrate ($R_{methane}$) under different rotating speeds (r , bottom axis) and corresponding Reynolds number (N_{re} , top axis) at 278.5 K and 7 MPa. Error bars indicate standard deviations of repeated measurements under identical experimental conditions. Reynolds number was calculated using the diameter of the impeller (18.66 mm) and the kinematic viscosity of water obtained from Refprop 9.0 software.

A moderate driving force (ca. 5 K sub-cooling) at 278.5 K and 7 MPa was selected and kept constant to investigate the effect of the mixing regimes. Reynolds numbers (N_{re}) for mixing is given by

$$N_{re} = \frac{r \cdot D^2}{\nu} \quad (3-1)$$

where N_{re} is the Reynolds number, r and D are the rotational speed (s^{-1}) and the diameter (18.66×10^{-3} m) of the impeller, ν is the kinematic viscosity ($\text{m}^2 \cdot \text{s}^{-1}$) of water obtained from Refprop 9.0 software. The initial linear rate (Figure 3.8 Regime II) was used to quantify the effect of mixing on the apparent formation rate of methane hydrates. Three different formation rate regions were observed when the rotating speed was increased from 630 rpm to 1300 rpm. The formation rate was relatively small when the speed was less than 800 rpm, when the hydrate layer was not refreshed by the moderate agitation, leading to a mass transfer

limited formation in Region A (See Figure 3.9). The formation rate was relatively slow, and methane hydrates accumulated at the liquid-gas interface.

When the speed was set between 800 rpm ($N_{re} \sim 3100$) to 1000 rpm ($N_{re} \sim 3900$) in Region B, a linear increase of the apparent formation rate was observed. It is likely that the fluid was in the transition regime where the agitation and turbulence were strong enough to remove the hydrate layer from the surface. The interfacial area was visually observed to be renewed continuously. The increase in apparent formation rate with agitator speed was attributed to the increased surface area of the free surface (surfaces of the vortex). In Region C, the formation rate was further increased by the strong agitation. However, the height of the reactor limited the further increase in the vortex size, contributing to a plateau of the formation rate at 1200 rpm. The stronger turbulence (above $Re \sim 4700$) also contributed to gas entrainment (See Figure 3.10), which substantially increased the liquid-gas interfacial area.

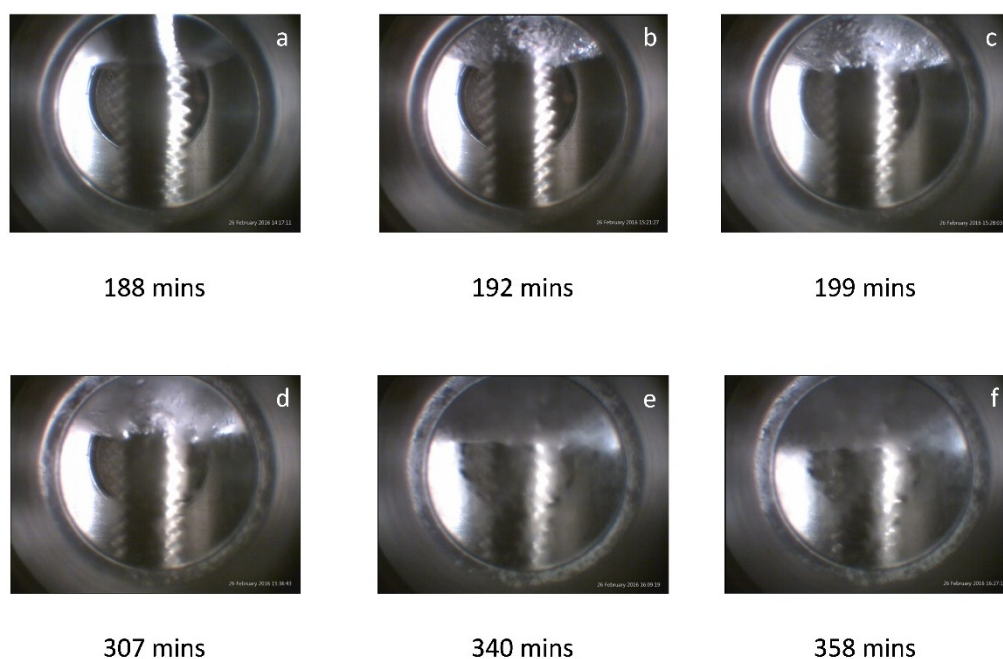


Figure 3.9 Hydrate formation at 278.5 K and 7 MPa with a rotating speed of 630 rpm. Time indicates the duration since the pressure and the temperature were stable. Figure a) shows the bottom of the vortex formed under weak agitation. The remaining pictures indicate the mass transfer limited hydrate growth.

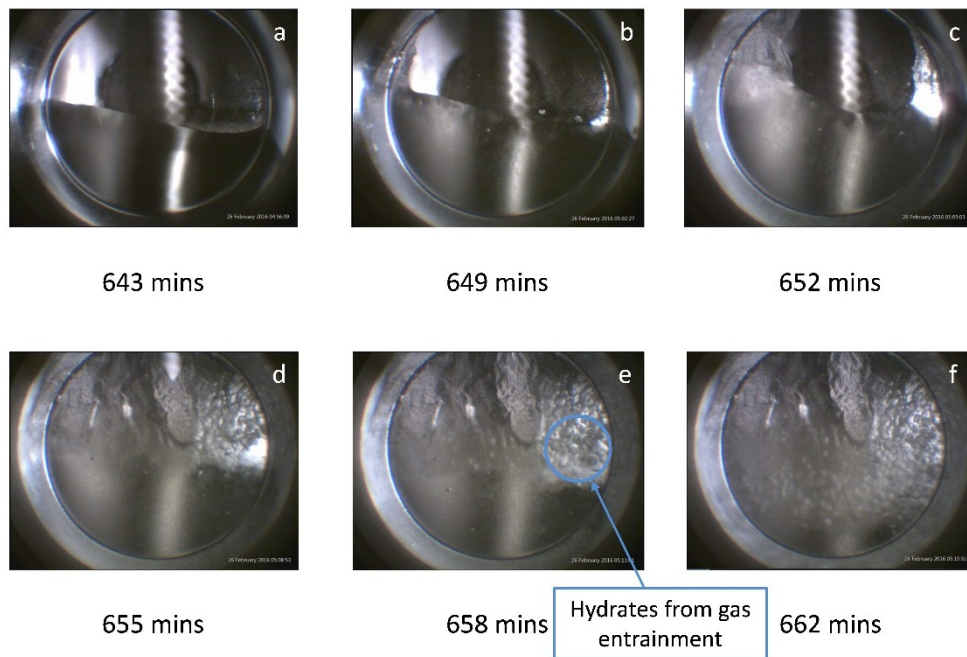


Figure 3.10 Hydrate formation at 278.5 K and 7 MPa with a rotating speed of 1300 rpm. Hydrates were formed by entrained CH_4 gas. Time indicates the duration since the pressure and the temperature were stable.

3.7.3 Impact of pressure-temperature conditions on the formation rates

A total of 69 formation experiments were conducted at temperatures from 276.5 to 283.5 K and pressures from 5 to 10.5 MPa in the binary $\text{CH}_4\text{-H}_2\text{O}$ system. The experimental results are summarised in Appendix A. The Regime II formation rates were calculated by averaging 2 to 3 measurements under identical conditions.

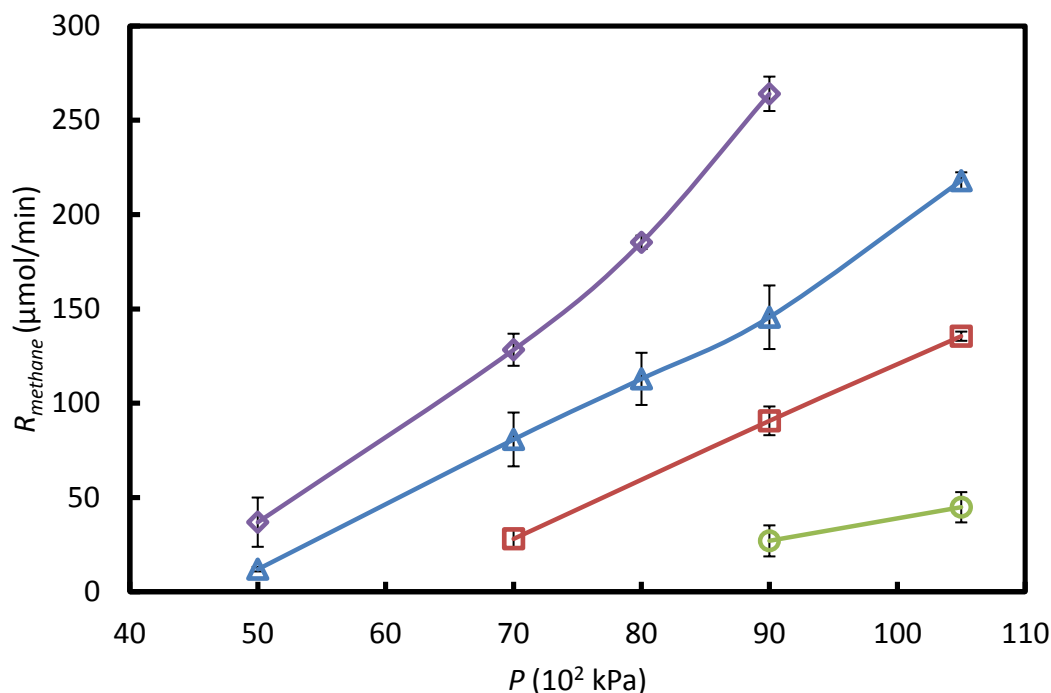


Figure 3.11 Regime II formation rates of methane hydrates (R_{methane}) under different pressures (P) at temperatures of $\diamond$, 276.5 K; $\triangle$, 278.5 K; $\square$, 280.5 K; $\circ$, 283.5 K. Error bars indicate standard deviations of repeated measurements under identical experimental conditions.

The driving force of the formation can be expressed as the degree of sub-cooling (ΔT , temperature below the equilibrium temperature of methane hydrates at representative pressures) or overpressures (ΔP , the difference between the equilibrium pressure and the experimental pressure at representative temperatures). The formation rate of methane hydrates increased non-linearly as a result of incremental increases of ΔT or ΔP particularly at the high driving forces, indicating that ΔT and ΔP might not be the appropriate driving forces to characterise the formation kinetics over a wide pressure/temperature range. The chemical potential difference, as an alternative driving force which includes both factors, will be discussed in the following section.

3.7.4 Impact of Chemical Potential on the Formation Rate of Methane Hydrates

The driving force for a new phase formation can also be expressed as the difference between chemical potentials of the old and new phases, sometimes called the supersaturation ($\Delta\mu$) [88]. Since the chemical potential of water vapour was negligible due to the slight amount present in the system, the chemical potentials of the old (precursor) phases are expressed as the

combination of μ_{dg} (dissolved gas) and μ_w (liquid water). If the chemical potential of each building unit (one gas molecule and n_w water molecules) of hydrates is μ_h , the supersaturation is given by

$$\Delta\mu = \mu_{dg} + n_w \cdot \mu_w - \mu_h \quad (3-2)$$

When the aqueous phase contacts with the gas phase for a long enough time, chemical equilibrium between the solution and the gas phase should be established, so that

$$\mu_{dg} = \mu_{gas} \quad (3-3)$$

μ_{gas} is the chemical potential of the gas phase. Therefore, at given pressure and temperature conditions, the equation can be rewritten as:

$$\begin{aligned} \Delta\mu &= \mu_{dg}(P, T) + n_w(P, T) \cdot \mu_w(P, T) - \mu_h(P, T) \\ &= \mu_{gas}(P, T) + n_w(P, T) \cdot \mu_w(P, T) - \mu_h(P, T) \end{aligned} \quad (3-4)$$

Under isothermal conditions, the following equations can be obtained from standard thermodynamic relationships [106] :

$$\mu_{gas}(P, T) = \mu_{gas,0}(T) + kT \ln[\varphi(P, T)P] \quad (3-5)$$

$$\mu_w(P, T) = \mu_{w,0}(T) + \int_0^P v_w(P, T) dP \quad (3-6)$$

$$\mu_h(P, T) = \mu_{h,0}(T) + \int_0^P v_h(P, T) dP \quad (3-7)$$

where $\mu_{gas,0}(T)$, $\mu_{w,0}(T)$, and $\mu_{h,0}(T)$ are the reference chemical potentials, $\varphi(P, T)$ is the fugacity coefficient of the gas, v_w and v_h are the volumes of water molecules and building blocks of hydrates crystal, respectively. Therefore, Eq. 3-3 yields:

$$\begin{aligned} \Delta\mu &= \mu_{gas,0}(T) - n_w(P, T)\mu_{w,0}(T) - \mu_{h,0}(T) \\ &\quad + kT \ln[\varphi(P, T)P] - \int_0^P v_w(P, T) dP + n_w(P, T) \int_0^P v_h(P, T) dP \end{aligned} \quad (3-8)$$

At hydrate equilibrium conditions, both the supersaturation and the chemical potential become zero.

$$0 = \mu_{gas,0}(T) - n_w(P, T)\mu_{w,0}(T) - \mu_{h,0}(T) + kT \ln[\varphi(P_e, T)P_e] - \int_0^P v_w(P_e, T)dP_e + n_w(P_e, T) \int_0^{P_e} v_h(P_e, T)dP_e \quad (3-9)$$

If the pressure dependence of hydration number, compressibility of aqueous phase and hydrate phase are negligible, the following relations hold:

$$n_w \approx n_w(P_e, T) \quad (3-10)$$

$$v_w \approx v_w(P_e, T) \quad (3-11)$$

$$v_h \approx v_h(P_e, T) \quad (3-12)$$

Eq. 3-8 can then be rewritten as:

$$\begin{aligned} \Delta\mu &= kT \ln \left[\frac{\varphi(P, T)P}{\varphi(P_e, T)P_e} \right] + \Delta v_e (P - P_e) \\ &= kT \ln \left[\frac{\varphi(P, T)P}{\varphi(P_e, T)P_e} \right] + (n_w v_w - v_{hydrate} / n_g)(P - P_e) \end{aligned} \quad (3-13)$$

where Δv_e is the difference between the water volume (v_w) of n_w water molecules and the volume of a hydrate building unit ($v_{hydrate}$) that contains n_g gas molecules. The subscript e denotes the properties at hydrate equilibrium conditions. The fugacity coefficient φ was obtained from the GERG-2008 model [107]. The equilibrium pressures (P_e) were calculated from the Sun and Duan model [108].

Figure 3.12 illustrates the formation rate of methane hydrates as a function of the relevant chemical potential driving force. The formation rates of methane hydrates at different isotherms collapsed into one exponential correlation, suggesting that the chemical potential gradient is suitable to be used as the driving force for methane hydrate formation compared to other supersaturation factors (i.e., the degree of sub-cooling and overpressures).

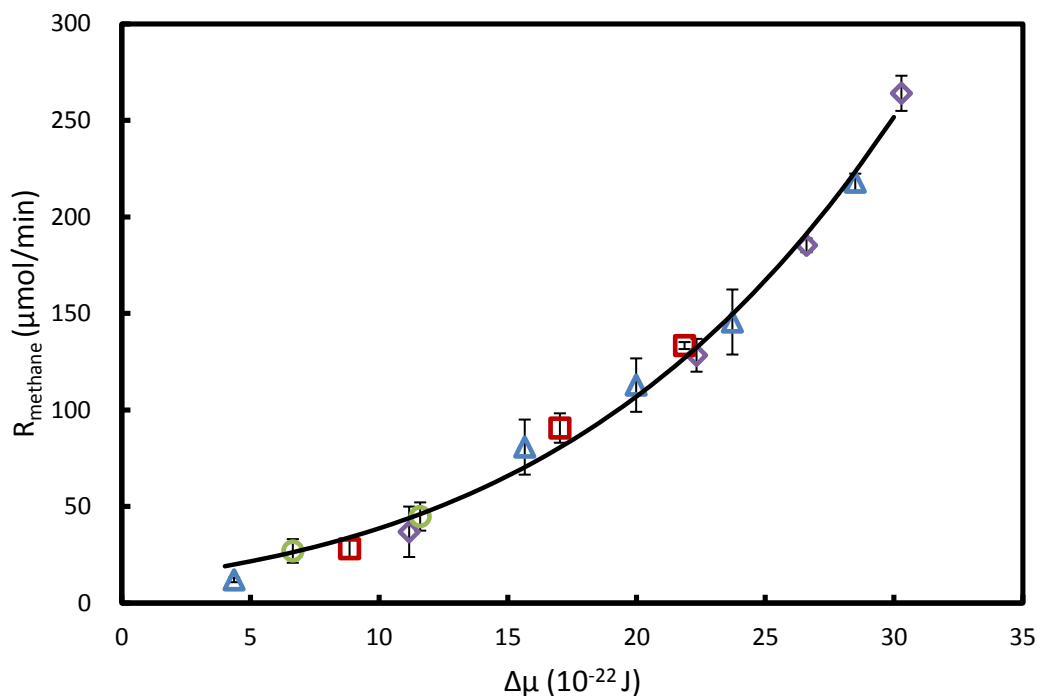


Figure 3.12 Correlation of hydrate formation rate (R_{methane}) and chemical potentials ($\Delta\mu$); $\diamond$, 276.5 K; $\triangle$, 278.5 K; $\square$, 280.5 K; $\circ$, 283.5 K; —, Exponential Correlation. Error bars indicate standard deviations of repeated measurements under identical experimental conditions.

The main source of variation of the measured formation rate was the downstream pressure control. Signification shifts (up to ± 0.03 MPa) of the reactor pressures were observed during the initial formation regime (Figure 3.5 Regime II). Taking into account the variations, the formation rates of methane hydrates still exhibited an exponential correlation with the chemical potentials under different conditions. The following section covers three modelling approaches that correlate the experimental data.

3.7.5 Comparison with Literature Data and Modelling Approaches

This study focused on the intrinsic formation rate of methane hydrate at the beginning of the hydrate growth regime. The most relevant studies were conducted by the Bishnoi group [64, 83, 84] and digitalised by Skovborg [85]. These formation kinetic data were widely accepted by different simulation models [109]. However, the original data from the Bishnoi group showed a relatively large scatter and error margins (see Figure 3.13).

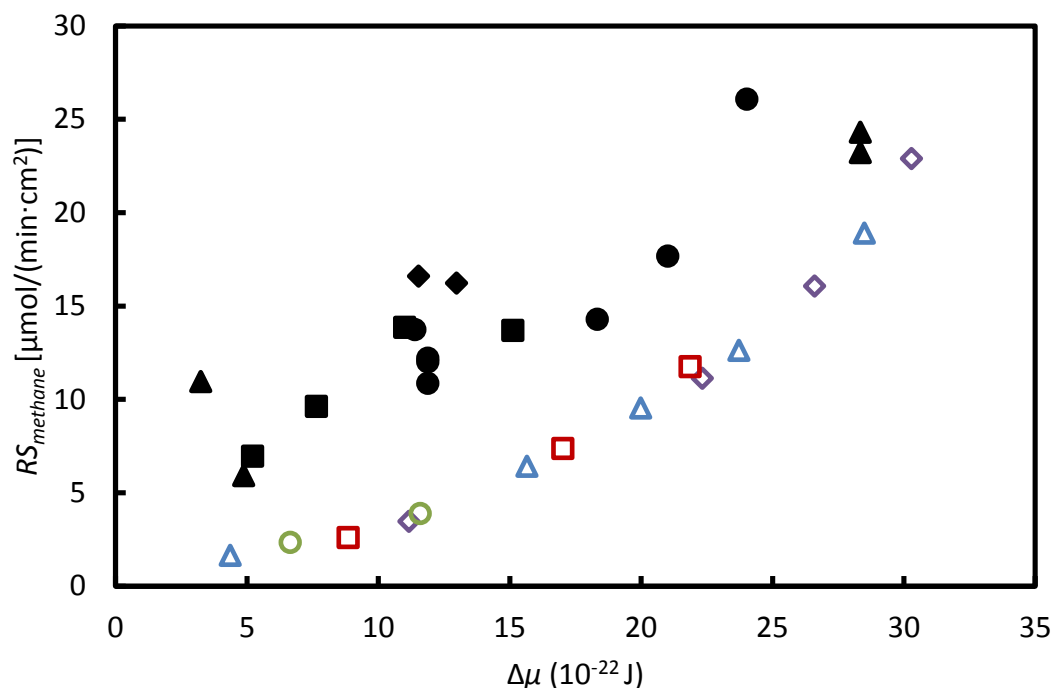


Figure 3.13 Comparison of hydrate formation rates ($RS_{methane}$) obtained from Bishnoi group [64, 83, 84] at $\blacklozenge$, 274 K; $\blacktriangle$, 276 K; $\blacksquare$, 279 K; $\bullet$, 282 K, and this study at $\blacklozenge$, 276.5 K; $\triangle$, 278.5 K; $\square$, 280.5 K; $\circ$, 283.5 K under different chemical potential differences ($\Delta\mu$). The formation rate was normalised by the interfacial area of $\text{CH}_4\text{-H}_2\text{O}$.

Both the literature data and the data from this study showed a similar increasing trend as the chemical potential difference increased. Such an increasing trend could be explained by the larger kinetic driving force of the gas hydrate formation under the larger chemical potential differences. As the displacement of the initial conditions from the phase boundary of methane hydrates increases, the chemical potential differences are expanded, leading to faster formation of methane hydrates. The results from this study suggest that the formation rate should not only have a simple correlation with the absolute temperatures but be a function of the kinetic driving force (i.e., chemical potential difference) of the process.

The formation rates of methane hydrates from this study and the data obtained by Bishnoi and co-workers [64, 83, 84] are within the same order of magnitude but the rates from this study are systematically smaller, which might be attributed to differences in the systematic errors of the measurements and the estimate of the liquid-gas interfacial area. The formation rate of methane hydrates is sensitive to temperatures (see Figure 3.11). A temperature difference of 2 K at 9 MPa leads to a two-fold increase in the formation rate from this study. In the work conducted by Bishnoi, the stated temperature error of 0.05 K from a Type T thermocouple greatly exceeds the accuracy provided by the manufacturer (Fluke, 0.35 K). Such a large uncertainty in temperatures could lead to a substantial error band in the determination of the formation rate. In this work, the liquid-gas interfacial area was estimated at ambient conditions, which may differ slightly at elevated pressures and low temperatures due to the difference in viscosity and interfacial energy. The temperature and pressure readings were carefully calibrated, but no subsequent validation was conducted. It would be meaningful to validate the accuracy of the measurement by conducting gas dissolution measurements (e.g., methane and carbon dioxide), with which existing literature data could be compared.

Three models were considered in this work. Two empirical models were used to correlate the formation rate and chemical potentials:

$$R_{methane} = e^{[a+b/(\Delta\mu+c)]} \quad (3-14)$$

$$R_{methane} = A \cdot \Delta\mu + B \cdot \Delta\mu^2 + C \cdot \exp(\Delta\mu) + D \cdot \Delta\mu^3 + E \cdot \Delta\mu^5 \cdot \exp(\Delta\mu) + F \quad (3-15)$$

A simple exponential correlation (Eq. 3-14) with three parameters was used to describe the exponential relationship between the formation rate and chemical potentials. The *AADP%* (Percentage absolute deviation between pairs)* of the exponential correlation was 11.4%. A polynomial based empirical correlation (Eq. 3-15) was also used to correlate the data with a reduced *AADP%* of 1.5%. The parameters of Eq. 3-13 and Eq. 3-14 are summarised in Table 3-1.

* Percentage absolute deviation between pairs

$$AADP\% = \frac{1}{N} \cdot \sum_{i=1}^N \left[\frac{R_{model} - R_{Experiment}}{R_{Experiment}} \right] \cdot 100$$

Attempts were also made to use a semi-empirical equation that was proposed by Vysniauskas and Bishnoi [64] to correlate the data (VB Model). The equation took into account an Arrhenius type of reaction rate constant, a temperature term and a pressure term with five parameters as shown in Eq. 3-15.

$$R_{methane} = A' \cdot \exp\left(\frac{B'}{T / K}\right) \cdot \exp\left(-\frac{C'}{(T_e / K - T / K)^{D'}}\right) \cdot (P / MPa)^{E'} \quad (3-16)$$

Vysniauskas and Bishnoi proposed that the second parameter B' was related to the activation energy (ΔE) of the hydrate formation and $B' = -\Delta E/R$, where R is the gas constant. The calculated activation energy based on the semi-empirical model from this work was 184.26 kJ/mol, which was similar to the activation energy obtained by Freer and co-workers (171 kJ/mol) [78] but larger than the value from Vysniauskas and Bishnoi (106.24 kJ/mol) [64]. However, during the optimisation process, it was found that mutual dependencies existed between the five parameters, which might lead to local optimal solutions based on the initial inputs. No attempts were made to obtain a similar activation energy, and one set of fitting parameters are summarised in Table 3-1.

Table 3-1 Parameters in Eq. 3-13, 3-14, and 3-15 for formation rate at temperatures from 276.5 K to 283.5 K and pressures from 5 MPa to 10.5 MPa for the binary CH₄-H₂O system

Parameters in Eq. 3-13 for the Exponential Model			
a	15.445	c	95.994
b	-1249.427		
Parameters in Eq. 3-14 for the Polynomial Model			
A	59.750	D	0.0499
B	- 2.804	E	5.571
C	3766.229	F	- 2.804
Parameters in Eq. 3-15 for the VB Model			
A'	7.68E-36	D'	2.51489
B'	22161.491	E'	2.86
C'	2.2351		

Figure 3.14 illustrates the absolute deviations of the three models from the experimental values. The polynomial model exhibited the smallest absolute deviations among the three models whereas the VB model showed the largest deviations from the experimental results. Again this illustrates the value of using $\Delta\mu$ as the single driving force. Equation 3.14 may be used to predict the Regime II hydrate formation rate from $\Delta\mu$ to within +5%.

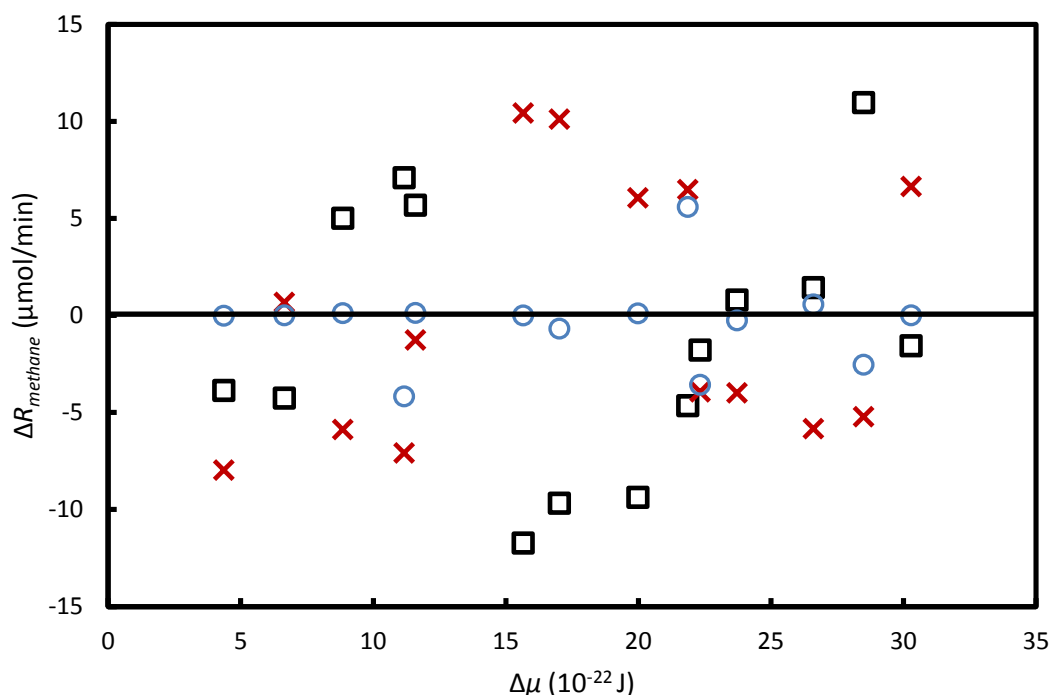


Figure 3.14 Absolution deviations ($\Delta R_{\text{methane}}$) between three models and the experimental data. Baseline represents the experimental value ($\Delta\mu$). $\times$, Exponential Model; $\square$, VB Model; $\circ$, Polynomial Model.

3.7.6 Impact of Surface Area and Water Physical State

The available surface area is another key factor that affects the apparent formation rate of methane hydrates. Dry water and micronised ice samples were used to investigate the effects of increased surface area on the formation rate of methane hydrates. Dry water samples consisted of micronised water droplets that were stabilised by functionalised silica particles in a gaseous environment (see Figure 3.15B) - the mass fraction of water was around 94 wt%; the droplet sizes were around 190 μm . By changing from bulk water into fine droplets on the micron scale, the surface area of the ‘Dry Water’ sample ($300.9 \text{ cm}^2\cdot\text{g}^{-1}$) increased

dramatically compared to that of the stirred bulk water system ($1.0 \text{ cm}^2 \cdot \text{g}^{-1}$). Similarly, the micronised ($\sim 7 \text{ }\mu\text{m}$) ice system has a further enhanced surface area of $16800 \text{ cm}^2 \cdot \text{g}^{-1}$.

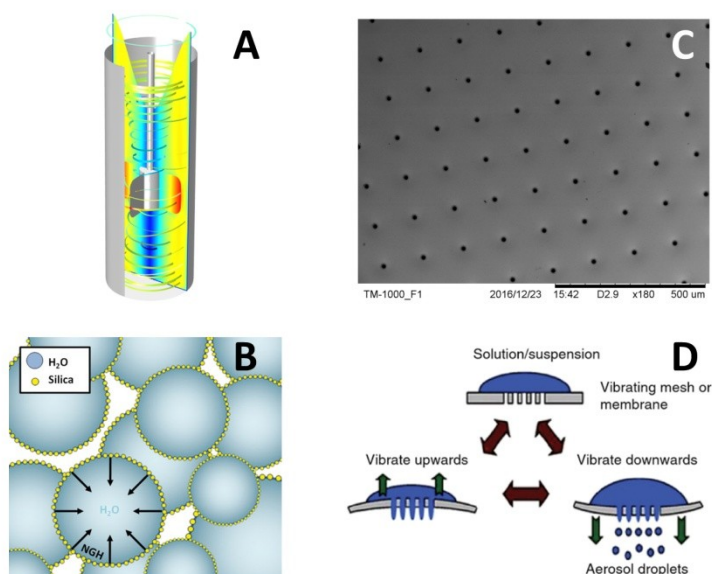


Figure 3.15 Illustrations of three different systems used in the formation kinetics study. A, the stirred water system, interfacial area formed by vortex; B, Dry Water “Reprinted with permission from Wang et al. [110]. Copyright (2008) American Chemical Society.”; C, SEM image of piezoelectric metal mesh with $7 \text{ }\mu\text{m}$ openings; D, Principles of piezoelectric atomiser “Reprinted from Anandharamkrishnan [111], Copyright (2011), with permission from Elsevier.”.

A total of 25 measurements were conducted for the formation rates of methane hydrates from Dry Water at 278.5 K and at pressures of 5, 7, 8, and 9 MPa. A total of 7 experiments were also conducted for the formation rate of methane hydrates from ice samples at 268 K and at pressures of 3, 4, and 6 MPa. The ‘Dry Water’ samples and the ice samples were prepared ex-situ as described in section 3.6 and transferred to the reactor before the experiments were conducted. All measurements with the ‘Dry Water’ samples and the ice samples were carried out without any agitation. The results are plotted in Figure 3.16. Li and co-workers [112] measured the average size distribution of the Dry Water formed by Aerosil R202, and concluded that the mean droplet size was $190 \text{ }\mu\text{m}$. Arpagaus [103] measured the droplet size distribution of water from a piezoelectric atomiser with a metal mesh that contained $7 \text{ }\mu\text{m}$ holes (See Figure 3.15 C and D). The size of the water droplets were $7.0 \text{ }\mu\text{m} \pm 0.5 \text{ }\mu\text{m}$. Taking into account of the density difference of water and ice at 293 K and 268 K, respectively, the diameter of the ice particles was estimated to be $7.2 \text{ }\mu\text{m} \pm 0.5 \text{ }\mu\text{m}$.

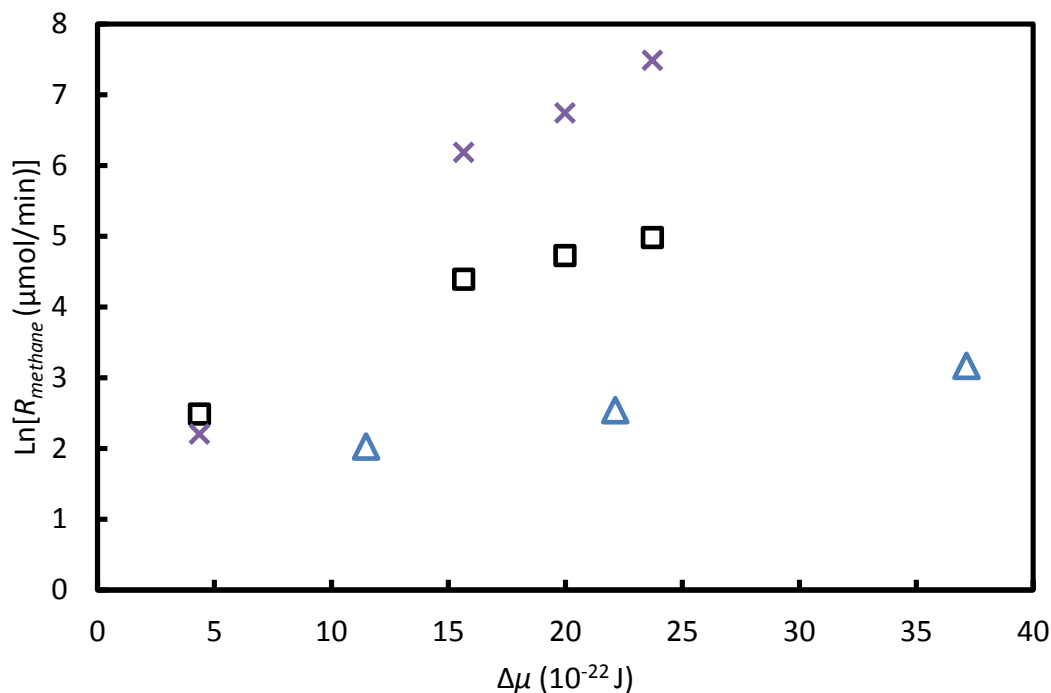


Figure 3.16 Natural Logarithm of methane hydrate formation rate (R_{methane}) at different chemical potentials ($\Delta\mu$). $\times$, Dry Water; $\square$, Stirred Water; $\triangle$, Ice.

Apart from the formation rate at small driving force ($\Delta\mu = 4.36 \times 10^{-22}$ J), the fastest formation rates were obtained from Dry Water samples, even in the stagnant system, whereas ice exhibited the slowest formation rates. Intermediate formation rates were obtained in the agitated bulk water system. The amplified formation rates of Dry Water were likely due to the increased available surface areas, on which silica particles acted as heterogeneous nucleation sites. Such nucleation sites have a major impact on the initial formation rates of methane hydrates.

The ratio between R_{DW} and R_{water} showed an increasing trend as the driving force increased. It is possible that the induction time also had an impact on the apparent formation rates. Water droplets in the Dry Water systems were separated from each other and could be treated as individual systems. At a small driving force ($\Delta\mu = 4.36 \times 10^{-22}$ J), the nucleation of methane hydrates might have different induction times, leading to a slow apparent formation rate from a partially reacted Dry Water system. When the driving force increased, the likelihood of nucleation increased and the apparent formation rate of Dry Water increased.

The melting points of methane hydrates from water and Dry Water samples were measured by a high-pressure differential scanning micro-calorimetry (HP- μ DSC); the detailed methods and operating procedures were documented in Chapter 4. Table 3-2 shows the equilibrium conditions of methane hydrates from bulk water and Dry Water hydrate samples.

Table 3-2 Melting points of methane hydrates from water and Dry Water samples

Pressure (MPa)	Melting Points of CH ₄ hydrates from water	Melting Points of CH ₄ hydrates from Dry Water (K)	Difference (K)
	(K)		
7	282.92	282.77	0.15
8	284.15	284.04	0.11
9	285.21	285.06	0.15

Park and co-workers reported that the equilibrium temperature of methane hydrates in Dry Water increased 1 K compared to that of bulk hydrates [113]. In this work, there was only a minor shift of the measured melting points (ca. 0.15 K) at three pressures (see Table 3-2). The difference in the change of melting points might be attributed to the different methods used for determining the equilibrium conditions. Park and co-workers used a continuous heating method for a relatively large amount of hydrate sample (100 g), which might introduce significant errors in the equilibrium measurements due to the metastability of methane hydrates and the low thermal conductivity of silica particles. In this study, such potential errors were overcome by using a much smaller sample amount (i.e., 50 mg in this study) and a slow heating rate (0.2 K·min⁻¹) in the DSC measurements.

The small differences in the melting points measured in this work would not be able to make a significant contribution to the overall formation rate. Unlike other thermodynamic hydrate promoters which were soluble in water, the silica particles only covered the surface of the water droplets, and the affected water molecules were only a small fraction of the total amount of water molecules present in the system. Therefore, instead of being thermodynamic promoters for hydrate formations, silica particles provide nucleation sites which promote the initial formation of methane hydrates.

Under a large driving force ($\Delta\mu > 15 \times 10^{-22}$ J), the formation rate of Dry Water increased 10 times compared to that of the agitated water system at 90 MPa ($\Delta\mu = 23.7 \times 10^{-22}$ J). The theoretical increase in the surface area was around 90 times or more (assuming spherical Dry Water droplet with a diameter of 190 μm). Hence, the increase in the observed formation rate of methane hydrates (ca. 10 times) in ‘Dry Water’ compared with agitated bulk water was much smaller than the magnitude of the increased surface area. It was observed visually that at elevated pressure, the volume of Dry Water reduced and coalescence of Dry Water particles might occur. Moreover, silica particles on the surface of Dry Water droplets reduced the available surface area. Assuming the intrinsic hydrate cage formation rate from the stirred water system and the Dry Water system at 90 MPa are the same, the surface coverage ratio of silica particles corresponded to 94.1 %, meaning that about 6 % of the water emulsion surface area was available for gas-water mass transfer.

Although the formation rates did not increase as much as the total surface area, the Dry Water system was able to achieve a high conversion (> 50 %) without any agitation (see Figure 3.17). The time required to achieve 60% conversion from the static Dry Water systems (in 220 minutes) was comparable to that from a stirred water system (210 minutes) with a high degree of mixing (1000 rpm) at 7 MPa and 278.5 K. The overall conversion rate of the Dry Water system depended on the driving force and the duration of the formation. Under four tested pressures, the overall conversion varied from 6.9 % to 80.7 %. The Dry Water system did not require any agitation during the formation process, which might be favourable for gas hydrate storage purposes [110]. The formation of methane hydrates in ‘Dry Water’ systems has been reported in the literature. However, past studies focused on the gas storage capacities of the ‘Dry Water’ system rather than measuring the initial formation rate of methane hydrates. The reported storage capacities of 175 v/v STP [110, 114] and 163 v/v STP [115] were higher than the storage capacity measured in this study (118 v/v STP), which might be attributed to the moderate driving forces used in this study.

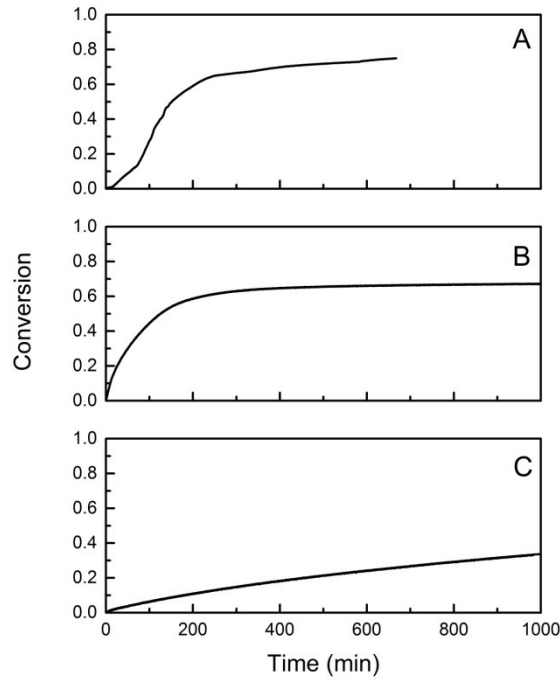


Figure 3.17 Conversion of water/ice into hydrates in three different systems. A, Stirred water at 7 MPa and 278.5 K with 1000 rpm; B, Dry Water at 7 MPa and 278.5 K; C, Ice at 6 MPa and 268.2 K.

The formation of methane hydrates from ice was a solid-state diffusion limited process and occurred relatively slowly compared to those from the stirred water system and the Dry Water system (See Figure 3.16 and Figure 3.17C). The reported rates corresponded to the initial 10 mol% conversion of the ice to hydrates. It is likely that the surface nucleation on ice was relatively slow in the solid-gas system (together with the slow diffusion of methane through both surface hydrate layers and the solid ice core), leading to the much reduced formation rate of methane hydrates in the ice system. The shrinking core model was also used to calculate the effective diffusion coefficient of methane gas into the ice powder [116]. In a diffusion limited reaction, the shrinking core model can be expressed as

$$D_e = \frac{\rho_{ice} \cdot R^2}{6 \cdot a \cdot C_{gas} \cdot t} \left[1 - 3(1-f)^{2/3} + 2(1-f) \right] \quad (3-17)$$

where D_e is the effective diffusion coefficient (m^2/s), ρ_{ice} is the density of ice (916 kg/m^3), R is the radius of the ice particle (m), a is the molar amount of ice required to form 1 mole of gas hydrate, C_{gas} is the density of methane (kg/m^3), t is the time required for converting 10 mol%

of ice into hydrates (initial formation rate) and f is the mole fraction of converted ice (0.1). Eq. 3-16 was used to calculate the effective diffusion coefficient of methane into solid ice particles. The measured formation rate of methane hydrate led to a diffusion coefficient of $2.07 \times 10^{-18} \text{ m}^2/\text{s}$. This calculated diffusion coefficient was two orders of magnitude smaller than the reported literature values of $5.83 \times 10^{-16} \text{ m}^2/\text{s}$ [117]. A few factors might give rise to these small diffusion coefficients. During the preparation of ice powders, it was found that the micronised ice powder did not preserve for a long period of time. An overnight storage of the ice powders at 263 K resulted in a consolidated block of ice. Therefore, ice powders were prepared freshly for each experiment. However, the time required for weighing and transferring the LN_2 cooled ice powder was around 10 to 15 minutes. Partial melting and consolidation were expected to occur, leading to reduced available surface area of ice powder. Due to the size of the ice powder, random packing of the ice powder resulted in a relatively low-permeability bed, and the reduced surface area due to packing and some fusion on contact was not considered in the shrinking core model. Moreover, during the formation process, aggregation and bridging of the micronised ice powder might further reduce the permeability, leading to a slower formation rate of methane hydrates. The value of $2.07 \times 10^{-18} \text{ m}^2/\text{s}$ should therefore be considered to be an effective diffusion coefficient for methane in this complex semi-consolidated hydrate-ice system.

3.8 Summary

In this work, formation kinetic measurements have been presented for methane hydrates in the temperature range 276.5 to 283.5 K and the pressure range 5 to 10.5 MPa. A piece of high-pressure apparatus was modified for conducting the formation kinetic measurements during the initial stage of hydrate formation at constant pressure and constant temperature conditions. The results showed that for bulk water the hydrodynamic conditions, especially the gas-liquid interfacial areas, were of key importance during the initial stage of the hydrate formation process. Low temperatures and high pressures promoted the formation of methane hydrates. It was also found that the formation rates of methane hydrates followed a simple approximately exponential trend with the chemical potential difference from the equilibrium

state for different (P , T) conditions. The measured formation rates of methane hydrate in the stirred water system agreed with the literature data to the same order of magnitude but showed a clear dependency on the chemical potential difference in the investigated pressure and temperature range. Such a dependency suggests that the displacement from the equilibrium conditions, regarded as a driving force of the hydrate formation (i.e., chemical potential difference), determines the initial formation rates of methane hydrates. An empirical polynomial model was proposed to correlate the formation rate of methane hydrates and chemical potential difference to within $\pm 5\%$.

The effect of surface area was also tested with the Dry Water system and the ice system, which have increased water surface areas of $300.9\text{ cm}^2\cdot\text{g}^{-1}$ and $16800\text{ cm}^2\cdot\text{g}^{-1}$, respectively, compared to that of the stirred water system ($1.0\text{ cm}^2\cdot\text{g}^{-1}$). The fastest apparent formation rate of methane hydrates was obtained from the Dry Water system, which showed a tenfold increase in the formation rates without any agitation compared with those from stirred water system. The fast formation rate in the Dry Water system was likely caused by the presence of silica particles, which acted as heterogeneous nucleation sites at the liquid-gas interface, as well as the increased available surface area for gas-water mass transfer. Comparing the formation rate of methane hydrates in the stirred water system and the Dry Water system, the net increase in the formation rate (ca. 10 times) was much smaller than the increase in the surface area (ca. 300 times), suggesting that the coverage of silica particles at the interface might reduce the available surface area for the hydrate formation. Comparing the increase in the surface area and in the formation rate gave a simple estimate of the surface coverage ratio of silica particles in the Dry Water system of 94.1%. Therefore only about 6% of the water droplet surface area was available for gas-water mass transfer.

The slowest formation rate of methane hydrates was observed in the ice system, which was around 10 times smaller than that from the stirred water system, despite the large surface area ($16800\text{ cm}^2\cdot\text{g}^{-1}$) generated by the micronised ice particles. The reduced formation rate in the ice system was likely caused by a slow nucleation process at the gas-solid interface in comparison with the liquid-gas interface in the stirred water system and the heterogeneous

solid-liquid-gas interface in the Dry Water system, and slow diffusion of methane through the hydrate layer formed on the surface of the ice particles and into the ice core. The presented formation rate of methane hydrates and the proposed correlation with chemical potential driving force, along with the quantification of the role of available gas-water surface area and diffusion within solid hydrate/ices, can be used as a benchmark for future formation kinetics studies (e.g., using different reactor configurations, different water precursor states or in the study of other gas hydrates).

Chapter 4

Phase Equilibrium and Kinetics of CH₄ Hydrates in Porous Media

4.1 Overview

Large amounts of naturally occurring methane hydrates are distributed on the continental shelf and in the permafrost region [16]. Significant portions of methane hydrates are deposited in porous media like clay or sandstone. Numerical simulation suggested that the hydrate-bearing sands and clay dominated reservoirs may be a feasible target for future energy production [11]. The equilibrium conditions of gas hydrate in porous media are important for estimating the amount of naturally occurring methane hydrates, locating the Bottom of Gas Hydrate Stability (BGHS) zones and interpreting the Bottom Simulating Reflector (BSR) data [118]. Therefore, the phase behaviour of methane hydrates in porous media is key to understanding the occurrence of methane hydrates in nature.

The objective of this part of work is to understand the phase behaviour of methane hydrates in well controlled porous media and provide a model to predict the phase behaviour of methane hydrates in the porous media. The formation and decomposition kinetics of methane hydrates were also measured in a static system. Another key output of this work is the impact of the surface chemistry of porous media. Studies of equilibrium conditions of methane hydrates in bulk and in porous media were conducted in a pressure range 5 to 50 MPa and in a temperature range 274 to 300 K, addressing the importance of pressure and temperature, pore size and surface chemistry.

4.2 Literature Review

Confinement in porous media affects phases transitions of fluids including the liquid-vapour phase transition and the liquid-solid phase transition [119]. When materials are confined in narrow pores, they exhibit different thermodynamic properties which differ from the macroscopic bulk properties. The confinement effect is due to the reduced dimensionality and strong material-wall interactions in the confined media [120]. If the liquid wets the internal walls of the confined media, the liquid phase is thermodynamically favoured in confinement. Macroscopically, reduced melting points and elevated boiling points of confined liquids are expected, for example, capillary condensation above the bulk vapour-liquid equilibrium conditions. The depression of melting points is also introduced as a result of the reduction in pressure in confinement. The reduced equilibrium pressure leads to a lower equilibrium temperature at which capillary-held liquid or vapour and bulk solid are in equilibrium [121].

Handa and Stupin [122] were the first to use laboratorially prepared porous silica to measure equilibrium conditions of methane and propane hydrates in porous media. They observed that the confined hydrate equilibrium pressures are 20% to 100% higher than those of bulk hydrates. The equilibrium temperatures and pressures for confined hydrates were determined by a stepwise heating isochoric method. The temperature in the system was raised stepwise in an increment of 0.5 to 1.0 K, and the equilibrium condition was determined by an inflection point on the pressure-temperature plot. Clarke and coworkers [123] proposed a thermodynamic model to predict the equilibrium conditions of gas hydrates in porous media. The predictive model incorporated the van der Waals and Platteeuw theory and assumed cylindrical pores required the input of the surface energy, mean pore radius and the wetting angle. Results from the model deviated from the data of Handa and Stupin by 16% for methane hydrates, which might be attributed to the large interfacial energy assumed (72 mJ/m²) and the assumption of a single pore size.

Uchida et al. [124, 125] utilised a similar experimental setup as Handa and Stupin [122] and conducted experiments with a wider range of pore radius. A continuous heating rate of 0.06

$\text{K}\cdot\text{h}^{-1}$ was used in an isochoric system. A depression of equilibrium pressures was observed for methane hydrates, carbon dioxide hydrates and propane hydrates. The shift of equilibrium temperature was inversely proportional to the pore diameter. Gibbs-Thomson equation was used to calculate the interfacial tension of water-ice system ($29 \pm 6 \text{ mJ/m}^2$), and two water-methane hydrate systems (39 mJ/m^2) [124]; ($17 \pm 3 \text{ mJ/m}^2$) [125]. They also concluded that the lower interfacial tension was caused by a wider range of pore diameters (6 different pore diameters).

Smith and coworkers [126] applied the stepwise heating isochoric method with porous silica of pores less than 7 nm. Due to the pore size distribution of the silica sample used, the pressure-temperature curve had a gradual change in slope, suggesting that hydrates in porous media melted over a temperature range instead of a single point. They proposed a mathematical model that incorporated the pore size distribution to interpret the pressure-temperature curve. Based on the model, hydrates were found to be uniformly distributed in all pores.

Seo and coworkers [127] used the continuous heating isochoric method with a slow heating rate of $0.1 \text{ K}\cdot\text{h}^{-1}$ to study the confined equilibrium of methane hydrates and carbon dioxide hydrates. A depression of equilibrium temperatures was confirmed by experimental data up to 10.5 MPa. The van der Waals and Platteeuw theory was used to model this experimental data. A correction term was applied to take into account the reduced water activity in confinement. The obtained data agreed well with those from Uchida et al. [124] but deviated significantly with those from Handa and Stupin [122] and Smith et al. [126]. Kang and coworkers [128, 129] used the same experimental and modelling method as Seo and coworkers [127]. A similar conclusion was made for the depressed melting points of confined methane hydrates and carbon dioxide hydrates. The additional NMR measurements also revealed that the structure of confined methane hydrates was the same as that of bulk hydrates.

Anderson et al. [130] improved the experimental accuracy by applying a differential thermal analysis to study the confinement effect of methane and carbon dioxide hydrates. The pressure range was extended to 14.07 MPa, and mesoporous silica with three different pore

diameters was used. Two temperature probes were in contact with porous media with hydrates and a reference fluid. A temperature inflation point was observed during the decomposition of hydrates due to the enthalpy of fusion of gas hydrates. In another paper by the same authors [131], they also examined the methods to test and interpret hydrate equilibrium data in confined geometry. It was concluded that the stepwise heating method was better than continuous heating method. The mean pore diameter could be used when a unimodal pore size distribution existed, and the dissociation data covered the whole range of the pore size distribution. It was also concluded that the enthalpy of fusion in confinement was not a strong function of pore sizes.

The impact of surface chemistry on the depression of melting points in confinement had been experimentally investigated for a range of systems, including ice in carbon nanotubes, ice in porous silica [132], and ice in functionalised porous silica [133]. The results suggested that the surface chemistry altered the melting points of ice in confinement. The degree of confinement effect depends on the material (fluid) – wall interactions. Depending on the type of interactions, the confinement effect can lead to elevated or depressed melting points, for example, oxygen in porous media showed elevated melting points [134]. Carbon tetrachloride also exhibited an increase in melting points in carbon nanotubes [135, 136] but a decrease of melting points in porous silica [137]. Further details can be found in three review articles [120, 121, 138]. However, the impact of surface chemistry in confinement for gas hydrates has not been properly addressed. Studies conducted by Riestenberg et al. [139] and Uchida et al. [140] suggested that mineral components and surface textures had a minor influence on the phase behaviour of methane hydrates, which might be attributed to the similar hydrophilicity of the tested materials.

The experimental conditions of the aforementioned literature of methane hydrates are summarised in Table 4-1.

Table 4-1 Literature experimental parameters of confined methane hydrates

	Pressure MPa	Temperature K	Pore Size nm
Handa and Stupin [122]	2.60 — 5.19	263.0 — 276.2	7
Uchida et al. [124]	4.80 — 8.50	277.2 — 283.7	10, 30, 50
Uchida et al. [125]	1.65 — 9.86	259.7 — 283.7	4, 6, 10, 30, 100
Smith et al. [126]	1.60 — 4.26	244.0 — 276.0	2, 3, 5, 7.5
Seo et al. [127]	4.01 — 10.50	275.3 — 284.5	6, 15, 30
Kang et al. [128, 129]	2.38 — 9.94	269.7 — 284.3	6, 30, 100
Anderson et al. [130]	3.69 — 14.07	271.8 — 287.5	9.2, 15.8, 30.6

Although considerable amounts of experimental data were collected, large discrepancies existed among the literature data, and the experimental data are limited to 14.07 MPa, which might not be a complete representation of the reservoir conditions for naturally occurring methane hydrates. Meanwhile, the importance of surface chemistry in confinement was not addressed in detail. It can be concluded that accurate measurements on the phase behaviour of methane hydrates in confinement are required at reservoir conditions up to 50 MPa. It is also important to investigate the impact of surface chemistry on confined methane hydrates, which are of importance for characterising naturally occurring methane hydrates in various reservoirs.

4.3 Apparatus

The core part of the high-pressure DSC apparatus (shown schematically in Figure 4.1) is a micro differential scanning calorimeter (Setaram, μ DSC Evo VII). Two Hastelloy cells were sealed by Nitrile Rubber or Hydrogenated Nitrile rubber O-rings (Polymax Ltd., BS006N70 and BS006HNBR70) and PTFE supporting gaskets (Virgin Grade, Homemade). Two cells, denoted as the sample cell and the reference cell, were enclosed in a two-stage Peltier thermal element controlled furnace. The temperature was recorded by 12 evenly distributed thermocouples around the sample cell and the reference cell. The heat flow resolution was 0.02 μ W. A thermostat (Julabo GmbH, F-33 EH) filled with circulated deionised water at 275 K dissipated excess heat from the furnace. Industrial grade nitrogen (BOC, Oxygen-free) was used as a purge gas to prevent condensation around the furnace. A high-pressure pump (Top-Industries, HP 50-1000) was used to deliver pressures up to 100 MPa at a constant

pressure mode or a constant volume mode. All process variables, including temperature, heat flow and pressures of the high-pressure pump were recorded by Calsto software (Setaram). A pressure transducer with a full-scale range of 100 MPa (Keller, PA-33X) recorded the system pressures via an RS485 cable. The voltage output of the pressure transducer was displayed by a readout unit (Keller, EV-06), and the digital output (RS485) was interfaced by a USB converter (Keller, K-114A).

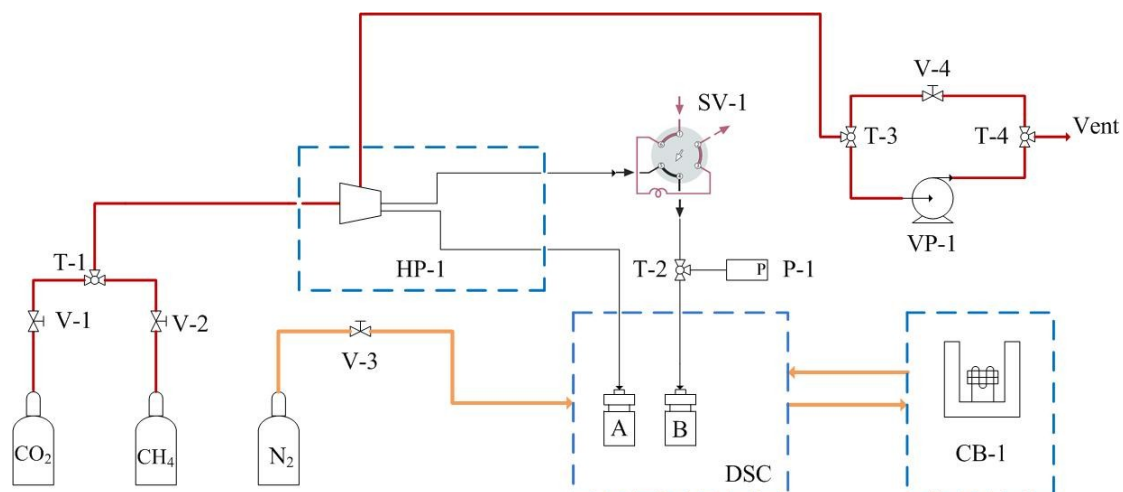


Figure 4.1 Schematic diagram of the high-pressure DSC apparatus: V-1, V-2, V-3 and V-4 manual valve; SV-1, high-pressure sampling valve; T-1, T-2, T-3 and T-4, tee connector; P-1, pressure sensor; HP-1, high-pressure pump; VP-1, vacuum pump; μ DSC, Differential Scanning micro-Calorimetry; A and B, reference cell and sample cell; CB-1, circulated cooling bath; — 1/16" high-pressure tubing; — 1/8" high-pressure tubing; — 1/4" low-pressure tubing

4.4 Materials

CP grade methane was supplied by BOC with a minimum mole fraction of 0.995. Industrial grade nitrogen provided by BOC was used as purging gas. Ultrapure Millipore water with an electrical resistivity higher than 18 M Ω ·cm at 298 K was deionised by using a Millipore-Q system. Silica-based Controlled Pore Glass (CPG, also known as Vycor Glass, Sigma-Aldrich) with different pore diameters were used in this study. Mesoporous carbon with a pore width of 10 nm $\pm$ 1 nm was purchased from Sigma-Aldrich. Toluene, Methoxytrimethylsilane and 3-Triethoxysilylpropylamine used for functionalisation of silica surfaces (Sigma-Aldrich, UK) were of purities 98%, 99%, and 97%, respectively. Mercury with a purity of 99.9995% was supplied by Mercury Recycling Ltd.

4.5 Calibration

Calibration of the temperature was conducted by using ultra-pure deionised water, certificated naphthalene, and mercury. In a typical calibration experiment for ice and mercury, 20 mg to 50 mg sample was placed in the sample cell, and the mass was measured by an analytical balance with 0.01 mg resolution (Mettler Toledo Ltd, PR5003). The furnace temperature was ramped down to 237 K and kept isothermally at 237 K for 30 minutes to provide sufficient time for nucleation of ice or mercury. The isothermal holding period was followed by a slow heating step from 237 to 293 K with a heating rate of 0.2 K·min⁻¹. For naphthalene, 4.02 mg of the certificated naphthalene sample was sealed into a stainless steel plug while a reference plug with the same weight was empty. During the naphthalene calibration experiment, the sample and reference plugs were placed into the sample cell and the reference cell, respectively. The furnace temperature ramped from 295 K to 373 K at a scanning rate of 0.2 K·min⁻¹, followed by a cooling step from 373 K to 295 K with the same ramp rate. The onset temperature, which was taken to be the intersection the heat flow baseline and the slope of the endothermic/exothermic peak (see Figure 4.4C), was regarded as the melting points of the sample. The uncertainty of the melting point measurement was estimated to be ± 0.08 K with a coverage factor of $k = 2$. Melting points of alkanes were found to be systematically higher (ca. 0.2 K) than their reported values, which might be attributed to dissolved gas. Due to high vapour pressures of the tested alkanes, degassing was impractical for the current setup.

The pressure transducer was calibrated with a high-pressure pneumatic calibrator (Fluke, PPCH-G) over the full range of 100 MPa. The expanded uncertainty of the pressure reading from RS 485 output was estimated to be ± 30 kPa with a coverage factor $k=2$.

4.6 Material Characterisation

Scanning electron microscopy (SEM) images were acquired on a Gemini 1525 FEGSEM scanning electron microscope instrument with a field emission gun. A bi-continuous

solid-void structure was observed for controlled pore glasses (see Figure 4.2), which was consistent with previous studies [141]. All the Vycor Glass samples shared a similar pore surface morphology.

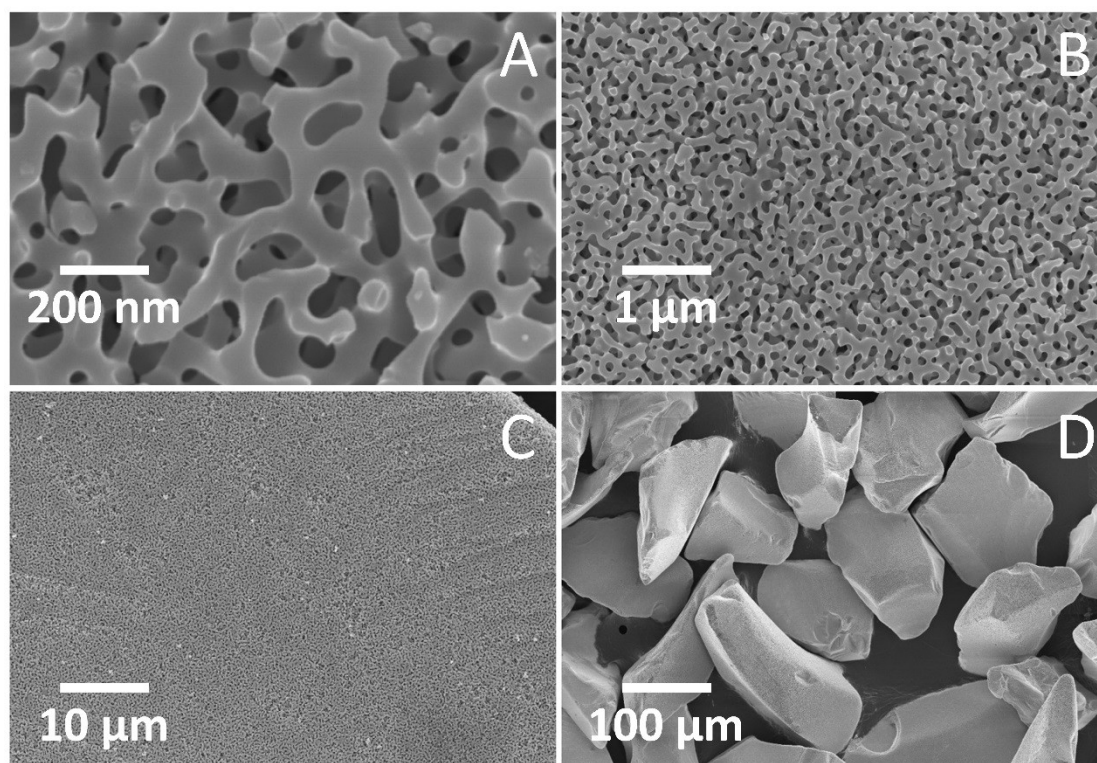


Figure 4.2 SEM images of the Vycor 196 sample: A, 100,000 times magnification; B, 25,000 times magnification; C, 5,000 times magnification; D, 500 times magnification

Mercury Intrusion Porosimetry (MIP) injection profiles over a pressure range of 0.0005 MPa to 227.49 MPa were recorded using an AutoPore IV 9500 (Micromeritics Instrument Corporation, USA) in order to determine the pore size distribution. A non-wetting contact angle of 130° and non-wetting (mercury) interfacial tension of 484 mJ/m² were assumed to convert the measured intrusion pressures into pore diameters for the different samples. Both mesopore and macropore (inter particle voids) intrusion was observed. Typical H1 type hysteresis loops [142] were observed for the six Vycor samples. The mean pore size of each sample was calculated by fitting the data to Gaussian peaks using Origin 9.0 software. Figure 4.3 shows the pore size distribution of the various Vycor materials.

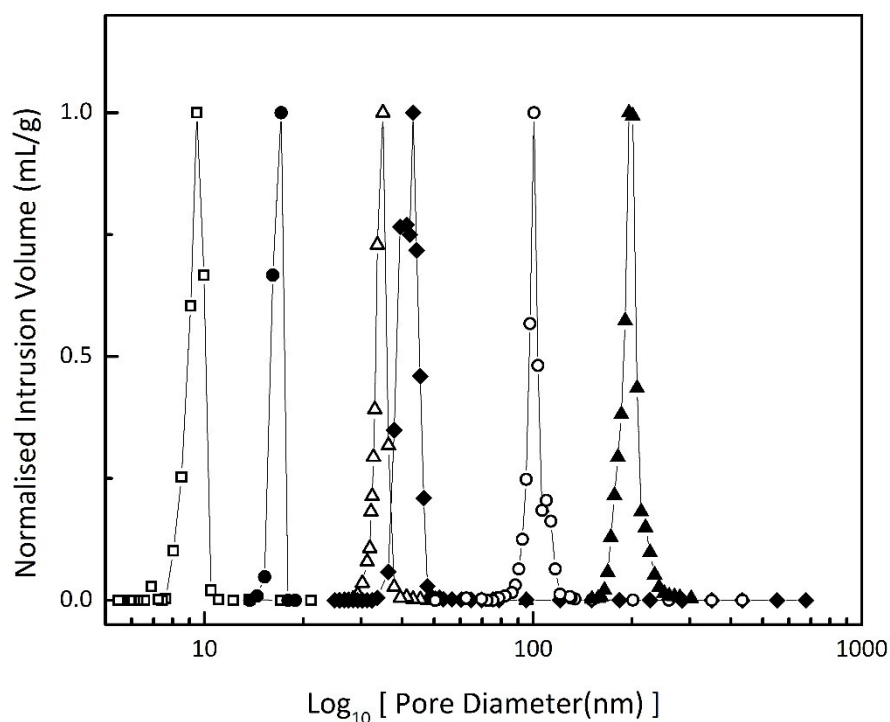


Figure 4.3 Intrusion volume versus calculated pore size of Vycor samples; $\square$, Vycor 8; $\bullet$, Vycor 17; $\triangle$, Vycor 35; $\blacklozenge$, Vycor 40; $\circ$, Vycor 95; $\blacktriangle$, Vycor 196.

Surface area was measured by nitrogen adsorption at 77 K with a Micromeritics Tristar 3000 device (Micromeritics, Norcross USA) from BET analysis and pore dimensions from BJH analysis [143]. Values of pore volume, calculated pore diameter, internal (pore) surface area, and particle size are summarised in Table 4-2.

Table 4-2 Physical properties of Vycor glass sample

Sample	Pore Size nm	Pore Volume mL/g	Surface Area m ² /g	Particle Size* μm
Vycor 8	8.5	0.40	162.42	74 – 125
Vycor 17	17.1	0.40	118.62	37 – 74
Vycor 35	34.8	0.72	59.23	74 – 125
Vycor 40	40.3	0.98	57.52	74 – 125
Vycor 95	95.4	0.79	25.96	74 – 125
Vycor 196	195.7	0.93	11.11	37 – 74

* Particle size is obtained from the manufacturer (Sigma-Aldrich)

4.7 Methods and Operating Procedure

4.7.1 Formation of methane hydrates in porous media

In a typical experiment, 50 mg silica and 20 to 57 mg water were loaded into the sample cell. The pore volume, which was measured as above by MIP, determined the amount of water loading required. 110% micropore-filling ratio was used for all mesoporous and macroporous silica samples. The system was subsequently sealed and evacuated by a vacuum pump under 0.8 kPa (BOC Edward, KNF-057500) for 30 minutes. The vacuum step not only removed air from the system but also facilitated water entering into the pores. Methane was subsequently introduced into the system and pressurised by the high-pressure pump to the elevated pressure. In a static system such as this micro-DSC, the formation rate of methane hydrates was very slow. Hence, an oscillating method was applied to accelerate the formation of methane hydrates [71]. The furnace temperature was firstly slowly cooled down to 243 K from room temperature with a ramping rate of 1 K·min⁻¹ and followed by 10 to 30 oscillating cycles between 243 K to 280 K with a scanning rate of 3 K·min⁻¹. The final stage was a dynamic heating step from 243 K to 303 K at a rate of 0.2 K·min⁻¹, designed to melt the now substantially 100% hydrate phase (see Figure 4.4).

A slow initial cooling step was found to promote the conversion of more water into hydrates at the first step. The repeated annealing process between 243 K and 280 K converted a small amount of water into hydrates in each cycle while hydrates remained (meta) stable during the whole process. During the final heating step, hydrates formed inside the pores and in the voids between particles (macropores) were melted and the heat flow during this process is shown in Figure 4.4B. The onset temperature of the endothermic peak was defined as the melting point of methane hydrates in the confined geometry.

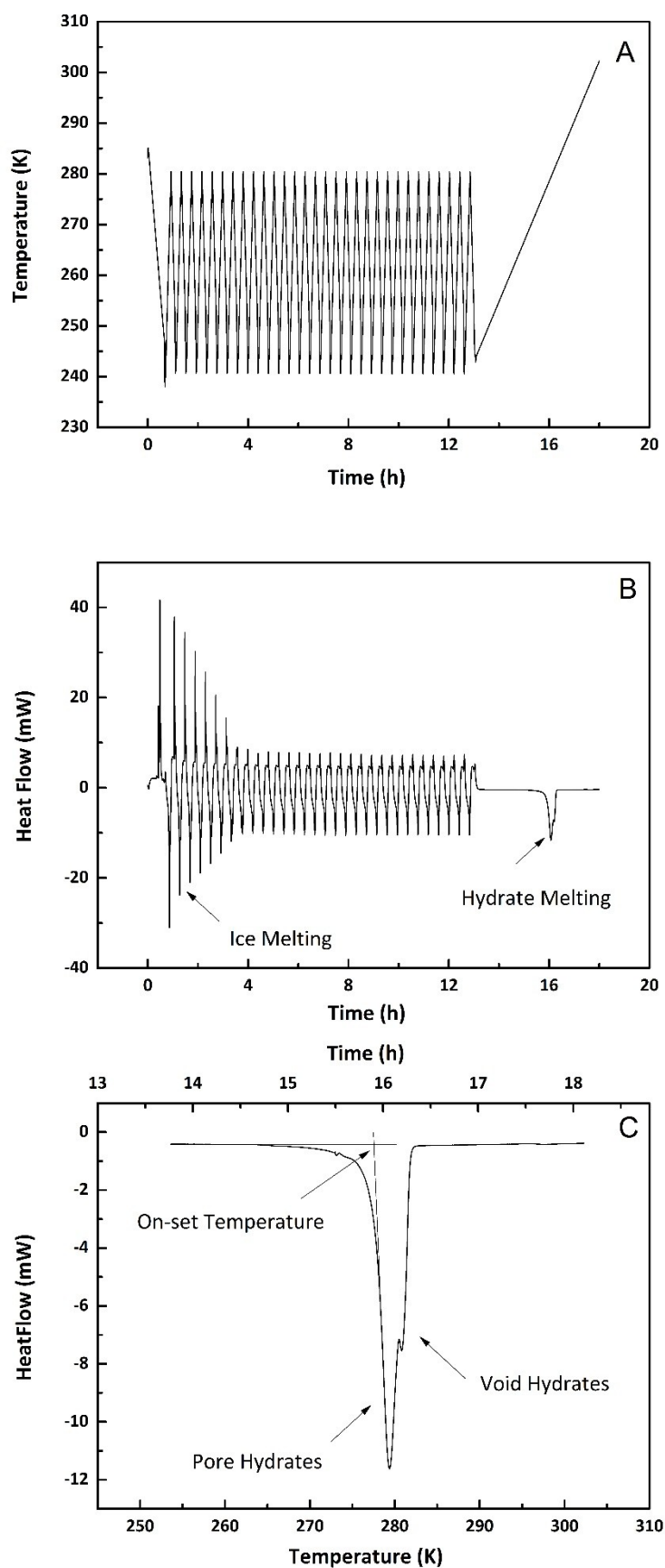


Figure 4.4 (a) Temperature profile during DSC experiment, (b) Heat flow during DSC experiment and (c) Endothermic melting peak of hydrates (expansion of hydrate melting section in plot (b)).

4.7.2 Impact of Particle Size

In the current setup, silica particles were randomly packed in the sample cell. Hydrate formation occurred at two different locations. Pore hydrates were formed inside the porous structure of silica particles, and void hydrates were formed in the void spaces between silica particles. Two types of hydrates are identified in the integrated heat flow peak during the decomposition process (see Figure 4.5). In order to measure the phase behaviour in confined geometries, accurately controlling the formation of methane hydrates between the void spaces of different particles played a significant role in the experiment. In theory, for a packed bed of particles, the inter-particle space ranges from ultra small pore to essentially bulk dimensions. Therefore, the effects of particle size along with the hydrates formed in the voids between particles was crucial to the accurate measurement of the phase behaviour of methane hydrates in the porous media.

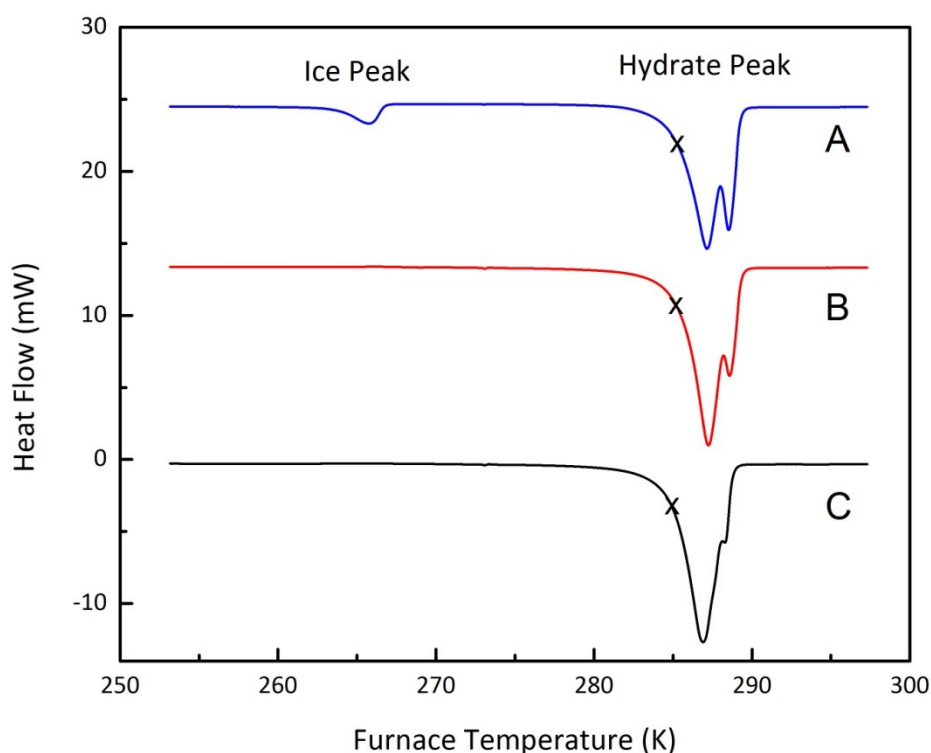


Figure 4.5 Effect of particle size on DSC melting peak shape with different particle sizes; A, 106 – 120 μm ; B, 53 – 75 μm ; C, 38 – 53 μm . (Experiments were conducted with Vycor 8 samples at 20 MPa. Onset temperatures are marked by crosses.)

Vycor 8 was used to investigate the particle size effect. The original particles were crushed and sieved by a series of stainless steel sieves (IMPACT Laboratory Test Sieve, UK). The particles were sieved into five different ranges, 38 μm – 53 μm , 53 μm – 75 μm , 75 μm – 90 μm , 90 μm – 106 μm , and 106 μm – 120 μm . The experimental procedure followed the protocol described in the previous section, working at a pressure of 20 MPa. Each experiment was repeated at least twice to check reproducibility.

As shown in Figure 4.5, the particle size did not affect the initial onset temperature of methane hydrate melting in porous media but altered the relative amount of methane hydrates formed in pores and in the macroporous void spaces between particles. For smaller particle sizes, much more hydrate was present in the pores than in the void space. Under the static (unstirred) experimental conditions employed, the surface of small particles with their larger surface area per unit volume (and hence the pores leading from their surfaces) were more accessible to the water. In the tested particle size range, less void hydrates were found as the particle size decreased. However, one should note that when the particle size was sufficiently small (i.e., less than 50 μm), the void hydrates have essentially the same melting point as pore hydrates. The effect of particle size on hydrate melting points was also confirmed for Vycor-95 particles.

4.7.3 Impact of Sample Mass

Excess water is essential to completely fill the pores of the sample. The effect of excess water was tested using Vycor 8 at 20 MPa with a heating rate of 0.5 K·min⁻¹. The pore volume data from MIP were used to calculate the mass of water to fill all the available pore volume. Following the protocol explained in the previous section, different amounts of water were injected into the system. Figure 4.6 shows the final decomposition heat flows after ten heating and cooling preparation cycles using different initial water contents.

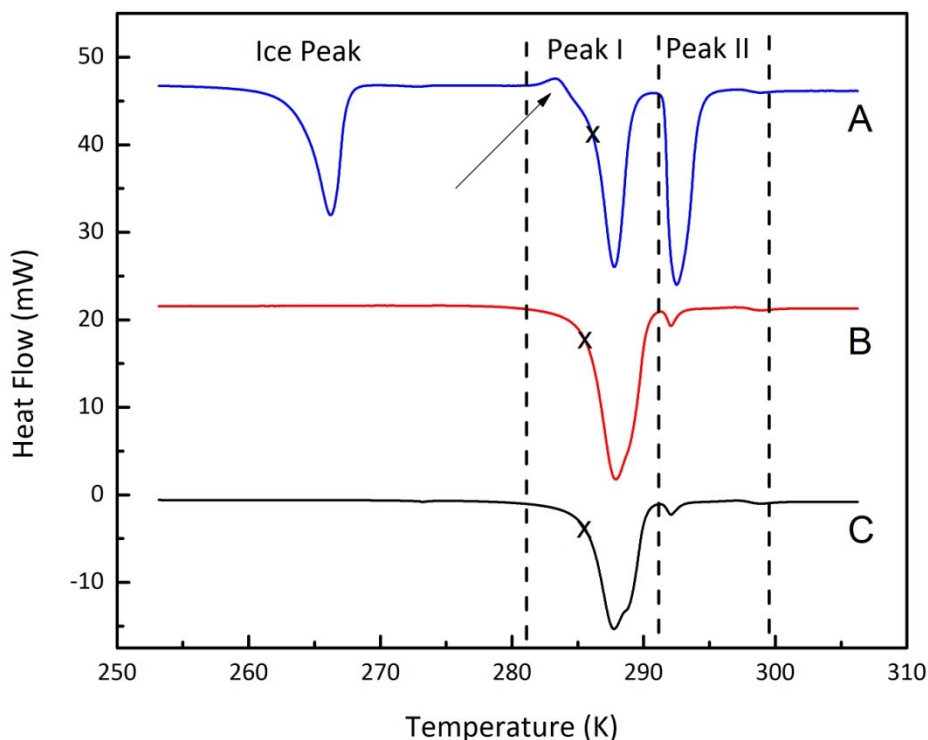


Figure 4.6 DSC melting peak shape of methane hydrates formed from different water loadings (Experiments were conducted with Vycor 8 samples at 20 MPa); A, 40.2 mg (200.9 % micropore filling); B, 19.8 mg (99.0 % micropore filling); C, 14.9 mg (74.5 % micropore filling). Onset temperatures are marked by crosses. Arrow shows a drifted baseline caused by hydrate formations.

As illustrated in Figure 4.6, Peak I denotes the pore hydrates, and bulk hydrates contribute to Peak II. When the amount of water increased, the area of Peak II increased. Although excess water contributed to enabling nearly full filling of the pore space, bulk hydrates and void hydrates affected the accurate interpretation of the pore hydrates' melting point. When the majority of heat flow came from void hydrates, the onset temperature was heavily influenced by the void hydrates (compare curve A - 40.2 mg water with curve B - 19.8 mg water in Figure 4.6). Even if deconvolution of overlapping peaks could resolve the actual onset temperature of the pore hydrates, it was not the preferred method. Meanwhile, excess water disturbed the baseline, leading to increased uncertainties in determining the onset temperature. Hence, the excess ratio was controlled at 110 % by water mass, which was large enough to resolve a slight indication of void hydrates without the latter peak markedly distorting the onset of melting of the pore hydrate.

4.7.4 Impact of Evacuation Duration

The sample containing the porous particles (Vycor 8) and water sample was maintained at vacuum (around 0.8 kPa) for 30 minutes. After the vacuum process, high-pressure methane was injected into the system and pressurised to the desired operating pressure. Pore capillary pressure, high-pressure gas and the initial vacuum conditions facilitated water entering into the pore structure. The melting peaks of hydrates indicated that the initial vacuum state promoted water occupying the pore volume, consequently leading to high pore hydrate to void/bulk hydrate ratio. Figure 4.7 shows the effect of vacuum and the absence of a vacuum process. Clearly, the pore/void hydrate ratio is markedly affected by the initial imposition of vacuum before the high-pressure gas injection.

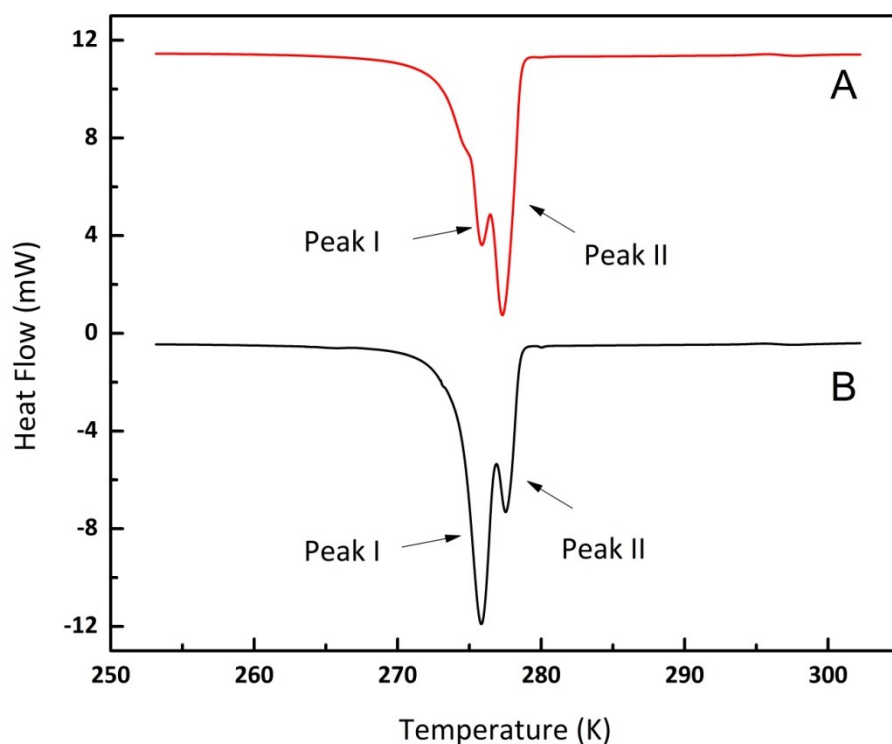


Figure 4.7 DSC Thermogram of methane hydrates using Vycor 8 samples formed at 5 MPa without the vacuum step (A) and with the vacuum step (B).

4.7.5 Impact of Formation Durations

In the absence of agitation, the conversion of water and gas into gas hydrates was a relatively slow process, which was governed by the small reaction rate at low temperatures and mass

transfer of gas into the liquid-solid phase. Hence, the oscillating heating cycle method was applied to accelerate the formation rate of methane hydrates. The annealing process took place between 243 K and 280 K. At the system pressure was above 5 MPa, a temperature of 243 K was sufficiently low to initiate the heterogeneous nucleation of methane hydrates and ice, whereas a temperature of 280 K provided sufficient temperature difference and heat to melt the unreacted ice, whilst leaving the higher melting hydrates in the solid state. Cooling back to 243 K converted some of the water into hydrate and as the number of heating-cooling cycles increased, the ratio of methane hydrates to unreacted ice increased .

The onset temperature of gas hydrate melting was independent of the number of heating cycles after full conversion achieved but depended on both the pressure and the pore distribution of the material. However, when the system reached a high conversion of water/ice into hydrates, the dominant large decomposition peak of gas hydrates enabled a more accurate determination of onset temperature. Additionally, it was observed that unreacted ice could form gas hydrates during the heating process, which caused an exothermic shift of the baseline (see Figure 4.6A shown by an arrow). The drifted baseline was also observed by Gupta and coworkers [144].

In order to avoid low conversions and baseline drifting, ten annealing cycles between 243 K and 280 K were used for experiments above a pressure of 15 MPa and 30 annealing cycles were used for experiments below that pressure. There was one exception for Vycor 8 at 5 MPa, where pore hydrates would melt at 280 K due to the very small pore size. The annealing cycle was therefore conducted between 243 K to 278 K for this condition.

4.7.6 Impact of Degassing and Memory Effect

Memory effects of gas hydrates have been widely observed in the literature [104]. In general, when hydrates were fully melted, it took less time to form hydrates again. This memory effect was also observed in mesoporous silica. It requires less annealing cycles to convert all water and/or ice into hydrates when a melted sample was used.

Although this memory effect had no impact on the melting point of pore hydrates and void hydrate, fresh silica and water sample were used for all experiments. In addition, Takeya and coworkers proposed that dissolved gas has a potential impact on the nucleation process of gas hydrates [104]. Due to the heterogeneity of the mesoporous silica system, such an effect was not observed here for deionised water with or without degasification.

4.7.6 Functionalisation of Silica Surfaces

Surface grafting of mesoporous silica was achieved by refluxing silica particle with organic silane through aqueous reactions. The functionalisation of silica surface was based on the procedure proposed by Luechinger and coworkers [145]. The mesoporous silica was firstly refluxed with water at 110 °C for 24 hours, and excess water from the pore surface was removed by drying the resulting particles at 105 °C in a vacuum oven (Thermo Scientific, UK) at 0.2 kPa for 48 hours, resulting in hydrolysed mesoporous silica from the water reflux method.

The hydrolysed mesoporous silica was suspended in toluene (100 ml/g). Different silanes (3-Triethoxysilylpropylamine 3.6 ml/g; methoxytrimethylsilane 2.8 ml/g) were added to the slurry and stirred for 14 hours at room temperature, resulting in amino porous silica and hydrophobic porous silica with high coverage ratio. Hydrophobic porous silica with low coverage ratio was synthesised by using methoxytrimethylsilane of 1.4 ml/g and reacted for 7 hours at room temperature.

A ‘super-hydrophilic’ surface of porous silica was fabricated by oxidising silica particles in an oxygen plasma using a plasma cleaner (PDC-32G-2, Harrick Plasma, USA). Silica particles were oxidised in a continuous air flow at 600 mTorr pressure with the flow rate maintained by a gas flow mixer (PDC-FMG), and the radio-frequency (RF) power set to 29.6 W for 2 hours.

4.8 Results and Discussion

4.8.1 Phase Behaviour and Enthalpy of Bulk Hydrates

Validation experiments were conducted to test the high-pressure DSC system by measuring the equilibrium temperatures of methane hydrates at a pressure range 5 to 50 MPa. The results (see Figure 4.8) were compared with the previously published literature data reported by Kobayashi and Katz [146], McLeod and Campbell [147], Marshall et al [148], Jhaveri and Robinson [149], Verma [150], Nakamura et al. [151], and Mohammadi et al. [152]. The obtained equilibrium data are in good agreement with the available literature data within the reported experimental uncertainties.

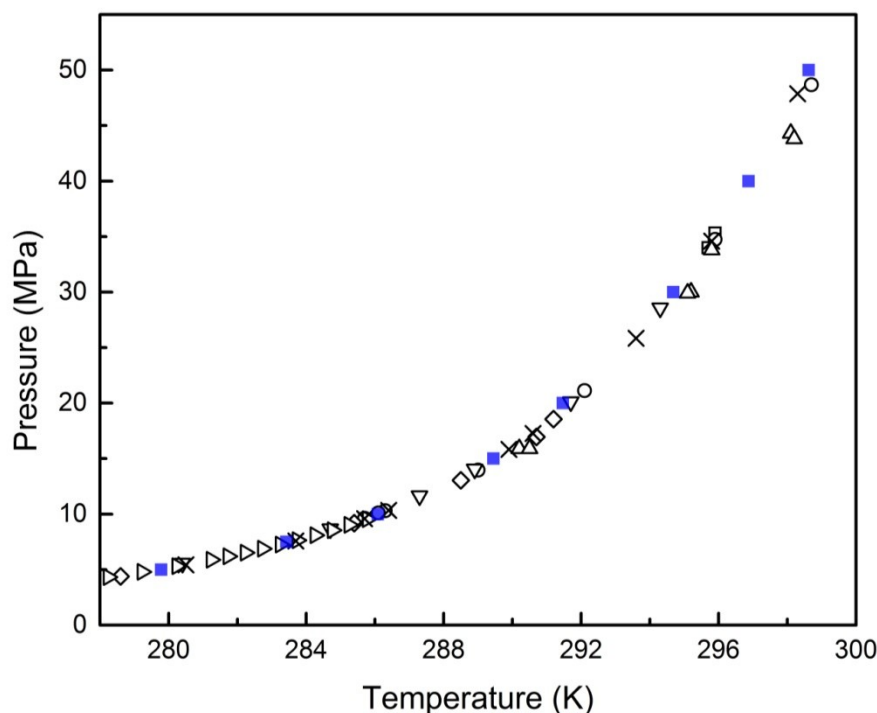


Figure 4.8 Equilibrium pressures of methane hydrates as a function of temperatures: ■, this work (Error bars are smaller than the symbols); □, Kobayashi and Katz [146]; ○, McLeod and Campbell [147]; △, Marshall et al. [148]; ▽, Jhaveri and Robinson [149]; ◇, Verma [150]; ▷, Nakamura et al. [151]; ×, Mohammadi et al. [152]

The experimental data were also compared with hydrate models (Duan model [108] and CSMHYD model [16]) and a commercial simulation software (Multiflash 6.0). Predictions from Duan model were in good agreement with the experimental data, whereas simulation results from Multiflash and CSMHYD under-predicted the equilibrium pressures of methane

hydrates at high-pressure conditions (see Figure 4.9). As suggested Sun and Duan [108], the CSMHYD model predicts hydrate equilibrium from Kihara potential with parameters fitted to experimental data. The model reproduces the fitted data to a good accuracy but has poor capabilities to be extrapolated beyond the fitted range. Therefore, the CSMHYD model at high pressures (above 40 MPa) becomes unreliable. An improved van der Waals-Platteeuw model with atomic site-site potentials from ab initio calculation was used in Duan model to account for the angle dependent molecular interactions. A comparison between the experimental data and predictions from Dual model gives a relative average absolute deviation $\Delta_{AAD\%} = 0.081\%$. Larger deviations were observed for results from Multiflash with $\Delta_{AAD\%} = 0.107\%$, and from CSMYD with $\Delta_{AAD\%} = 0.331\%$.

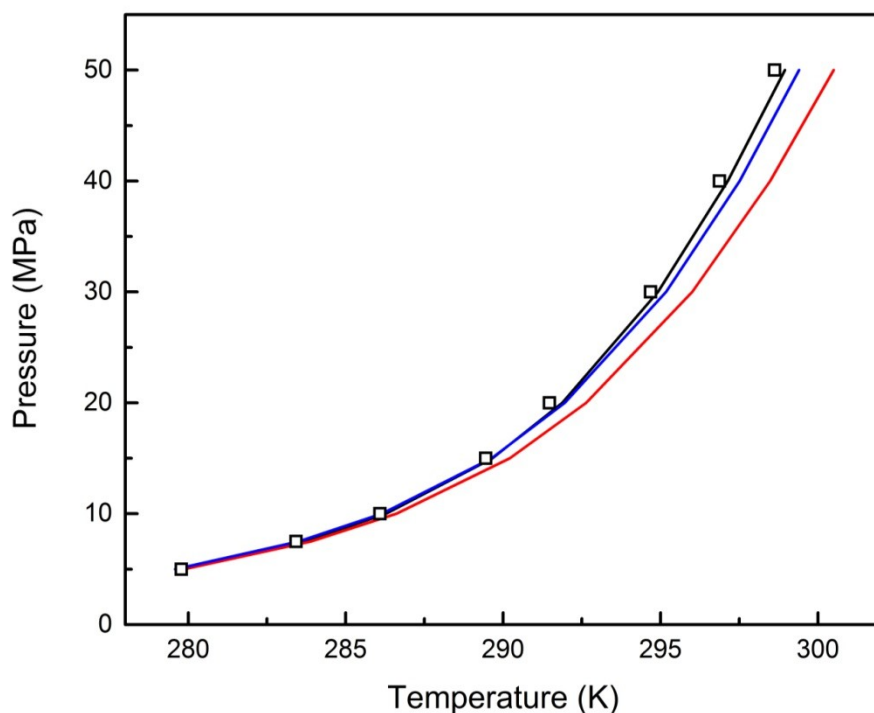


Figure 4.9 Prediction of equilibrium pressures of methane hydrates and experimental values: $\square$, experimental data (Error bars are smaller than the symbols); —, Duan Model; —, Multiflash 6.0 software; —, CSMHYD model

Enthalpy of fusion is known to vary with temperature. Regarding methane hydrates, elevated pressures lead to the higher melting point that may affect the enthalpy of methane hydrates' decomposition. A few experimental values were reported at low pressures [153-155] and Gupta et al. performed the enthalpy measurements up to 19.3 MPa [144], but there are no

experimental data available above 20 MPa. The enthalpy of methane hydrates' fusion was measured at pressures of 5, 10 and 40 MPa using an improved experimental procedure.

To accurately measure the enthalpy of fusion of methane hydrates calorimetrically, two factors are of importance: an accurate initial water content and fully converted hydrate samples. During the melting process of methane hydrates, partially converted methane hydrates show a secondary hydrate formation during the heating step, which causes an exothermic shift of the heat flow. The shifted baseline led to difficulties in determining accurately the boundary conditions when the peaks were deconvoluted and integrated. Fully converted hydrates were therefore obtained by using a small amount of sample mass (ca. 5 mg) and extra numbers of temperature oscillating cycles (ca. 20 to 30).

Due to the small amount of sample mass, accurate gravimetric measurements of small quantities in a relatively heavy reactor (ca. 14.5 grams) were difficult and evaporation of water during the measurement also compounded the uncertainties. Therefore, the mass of the initial water content was determined calorimetrically from the area under the DSC ice melting peak by using the ice enthalpy of fusion (333.43 J/g [156]) at ambient pressure. The experimental values are summarised in Table 4-3.

Table 4-3 Enthalpy of methane hydrate dissociation at different pressures

Pressure (MPa)	Enthalpy of fusion (J/g-water)	Enthalpy of fusion* (J/mol-gas)
5	494.8 ± 2.0	53.5 ± 0.5
10	500.7 ± 3.9	54.1 ± 0.4
40	503.8 ± 4.4	54.5 ± 0.5

*Hydration number was assumed to be $n = 6$

The obtained value was in good agreement with literature values, 53.87 ± 1.45 J/mol-gas at 12.8 MPa [144], 54.19 ± 0.28 J/mol-gas at 0.1 MPa [153], 54.84 ± 0.89 J/mol-gas at 0.1 MPa [155] and 52.5 ± 1.7 J/mol-gas (calculated from Clapeyron equation) [157]. In the investigated pressure range, the enthalpy of fusion of methane hydrates showed a minor dependency on the pressure/temperature, which was consistent with the thermodynamic expectations for enthalpy properties.

4.8.2 Formation and Decomposition Kinetics of Gas Hydrates

Due to the lack of agitations in a static (unstirred) system like the high-pressure DSC, both intrinsic formation rate of methane hydrates and mass transfer coefficients affect the overall formation rate of methane hydrates. The conversion ratio of water into methane hydrates was quantified by the amount of ice melted in each temperature cycles (see Figure 4.10).

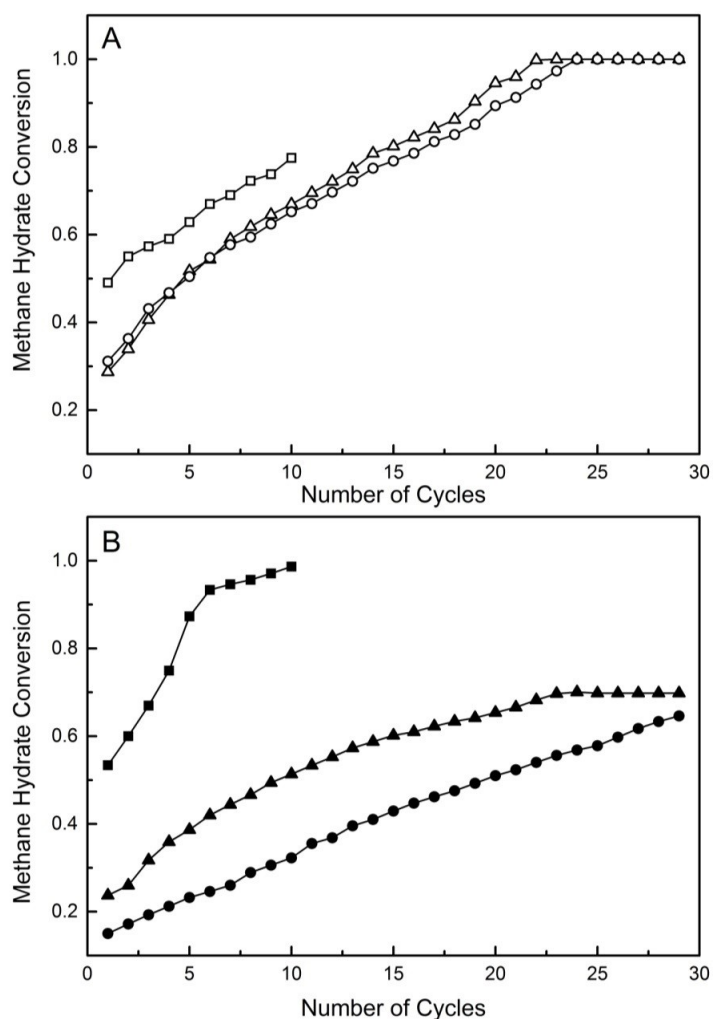


Figure 4.10 Methane hydrate conversion during temperature oscillating cycles in different media: A) in Vycor 40; B) bulk hydrates; $\square$, 40 MPa in porous media; $\triangle$, 20 MPa in porous media; $\circ$, 10 MPa in porous media; $\blacksquare$, 40 MPa from bulk; $\blacktriangle$, 20 MPa from bulk; $\bullet$, 10 MPa from bulk

It was assumed that water was converted into either hydrates or ice during the temperature cycles and heat of fusion of ice was 333.43 J/g. The sample mass of water was 40 ± 0.1 mg in all measurements presented in Figure 4.10 and 50 mg of Vycor 40 was used as the porous media. At 20 MPa and 10 MPa, high conversions were observed in porous media. Both initial

conversion ratio (amounts that were converted in the first temperature cycle) and final conversion ratio (amounts converted at the end of the experiments) were higher in porous media than those in bulk. The promotion was attributed to the increased surface area. At 40 MPa, the formation rate in bulk out rated the formation rate in porous media, indicating that high initial conversion ratio (ca. 50 %) might lead to a partially blocked porous network.

It was also observed that melted samples required less number of cycles to achieve full conversion of hydrates. The droplet shape of the initial water for bulk hydrates, which determined the interfacial area of the reaction, also had minor effects on the formation rate. Small particle sizes of the porous silica promoted the formation rate of methane hydrates, suggesting that the connectivity of the porous network and the diffusivity of methane through the porous media would affect the overall formation rate of methane hydrates.

Gas hydrates may show metastability phenomena under certain conditions where gas hydrates preserve their stability outside the stable region of gas hydrates [158]. When the surrounding conditions of gas hydrates change (i.e., pressure changes), the intrinsic metastability of gas hydrate may require a certain amount of time to regain the equilibrium. The effect of different formation and decomposition pressures was tested at 6, 12, 20, and 30 MPa for CO₂ hydrates (see Figure 4.11). Diamond symbols represent CO₂ hydrates formed and melted at the same pressure. For other symbols, hydrates were formed at 30 MPa by the temperature oscillating method and melted at lower pressures with various durations of isothermal holding before melting.

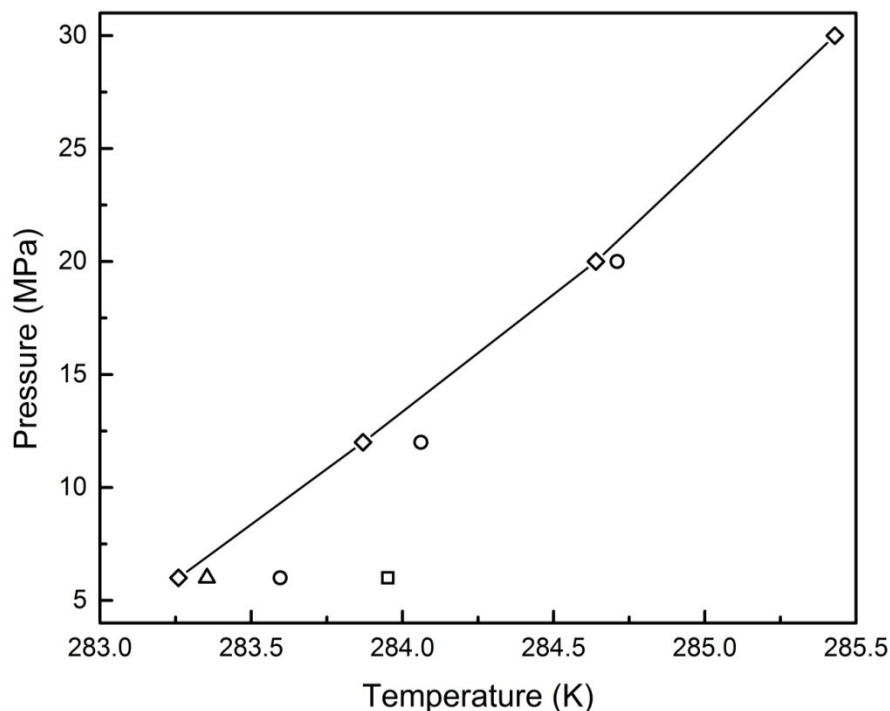


Figure 4.11 Metastability effect on equilibrium pressures of CO₂ hydrates as a function of temperature: ◇, hydrates formed and melted at the same pressure; □, hydrates formed at 30 MPa and melted at 6 MPa without an isothermal holding period; ○, hydrates formed at 30 MPa and melted at different pressures with an isothermal holding period of 0.5 hours; △, hydrates formed at 30 MPa and melted at 6 MPa with an isothermal holding period of 6 hours

Temperature hysteresis was observed when the pressure was reduced before melting commenced. A maximum difference of 0.96 K was observed when the pressure was reduced from 30 MPa to 6 MPa and hydrates melted without isothermal holding at 253 K. Long isothermal holding periods at 253 K were found to minimise the temperature hysteresis. It was likely that hydrate crystals formed at high-pressure conditions contained large internal stress and the stress relaxation process required a relatively long period.

4.8.3 Melting Points of Confined Ice

Melting points (T_m) of confined ice in mesoporous media have been extensively investigated by various techniques, including NMR spectroscopy [159], neutron diffraction [160], differential thermal analysis [130], and calorimetry [125].

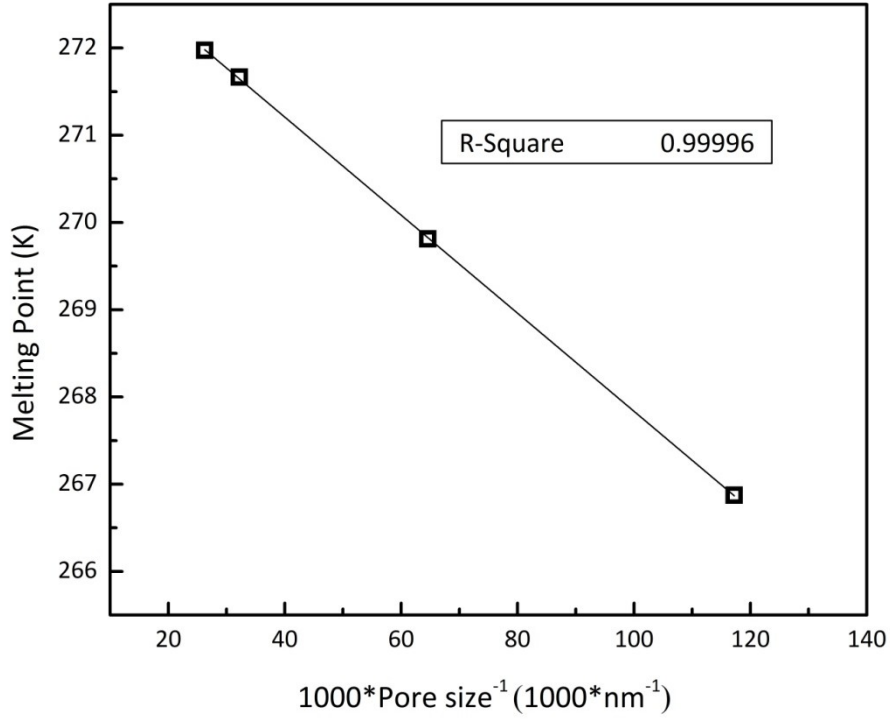


Figure 4.12 Confined melting points of Ice in porous silica

The experimental results obtained in this study are plotted in Figure 4.12, where confined melting points of ice are plotted versus the reciprocal of the mean pore width. It is seen that Figure 4.12 is consistent with the Gibbs-Thomson equation (G-T equation) [161].

$$\frac{T_{mb} - T_{pore}}{T_{mb}} = \frac{2 \cdot \gamma}{\Delta H_{fus} \cdot \rho_{ice} \cdot r_{pore}} \quad (4-1)$$

where γ , ΔH_{fus} , ρ_{ice} , and r_{pore} represent the interfacial energy, enthalpy of hydrate fusion, density of hydrates, and pore width, respectively. T_{mb} and T_{pore} are the melting points of ice in bulk and porous media. A fully wetted contact angle was assumed. Density of bulk ice $\rho_{ice} = 916 \text{ kg/m}^3$ and bulk ice enthalpy of fusion $\Delta H_{fus} = 6.01 \text{ kJ/mol}$ were used. The interfacial energy of ice/water surface from this study $31.4 \pm 1.5 \text{ mJ/m}^2$ was in good agreement with the literature values of $29 \pm 6 \text{ mJ/m}^2$ [125], $32 \pm 2 \text{ mJ/m}^2$ [130] and $31.7 \pm 2.7 \text{ mJ/m}^2$ [162].

4.8.4 Phase Equilibrium of Methane hydrates in confined media

The melting points of methane hydrates at eight isobars were investigated in the present work over the pressure range 5 to 50 MPa and pore size range 8.5 to 195.7 nm. Melting points of methane hydrates in bulk were also measured under comparable conditions. The reproducibility of the hydrate melting temperature was within ± 0.1 K. The results are summarised in Appendix B and plotted in Figure 4.13.

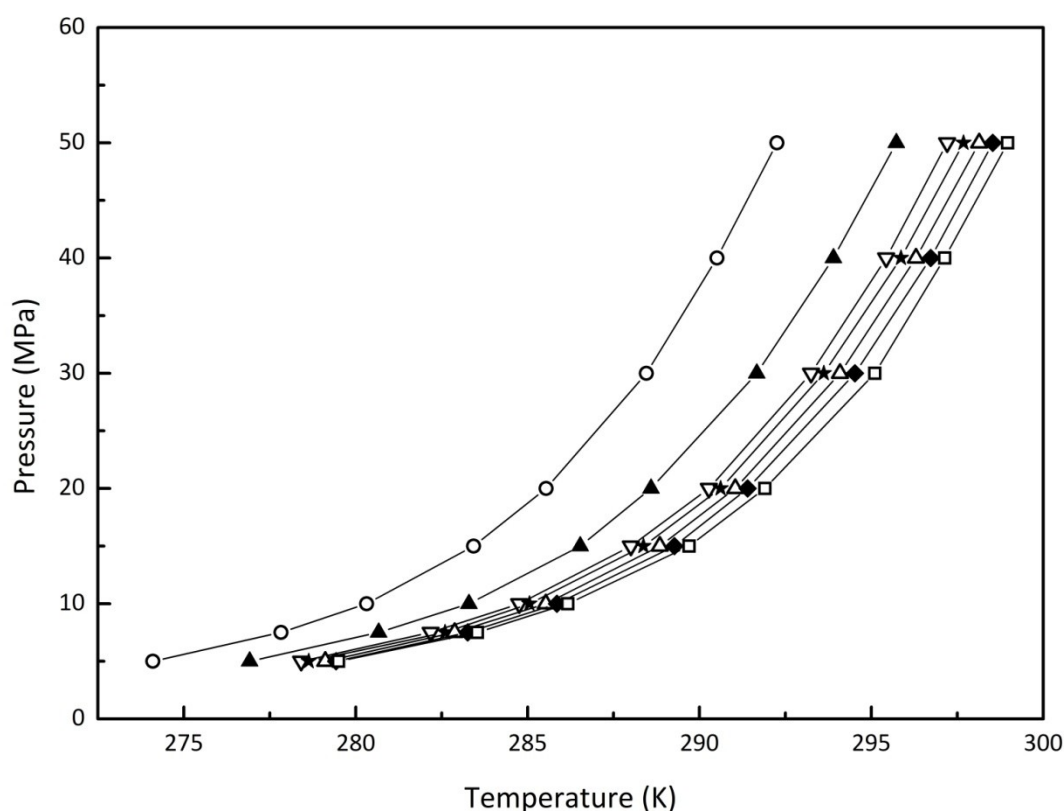


Figure 4.13 Melting points of methane hydrates in a range of porous particles and in the bulk (Error bars are smaller than the symbols); ○, Vycor 8; ▲, Vycor 17; ▽, Vycor 35; ★, Vycor 40; △, Vycor 95; ◆, Vycor 196; □, Bulk hydrates

Overall a significant decrease of the melting point was observed in the confined mesoporous and macroporous silica, consistent with earlier work [130] and with thermodynamic expectations. As the pore size decreased, the melting point of the pore hydrates decreased. This depression of the melting point was also observed to be pressure dependent, the effect being more pronounced at higher pressures. The trend of the pore hydrate melting points with pressure was consistent with that for bulk hydrates, which increased essentially exponentially

with increase of the pressure. The pore inhibition effect became far less significant for pore sizes larger than 200nm. Melting points of methane hydrates in another macroporous sample (pore size around 300 nm) showed identical melting points as bulk hydrates at the same pressure.

4.8.5 Interfacial Energy and the Gibbs-Thomson Equation

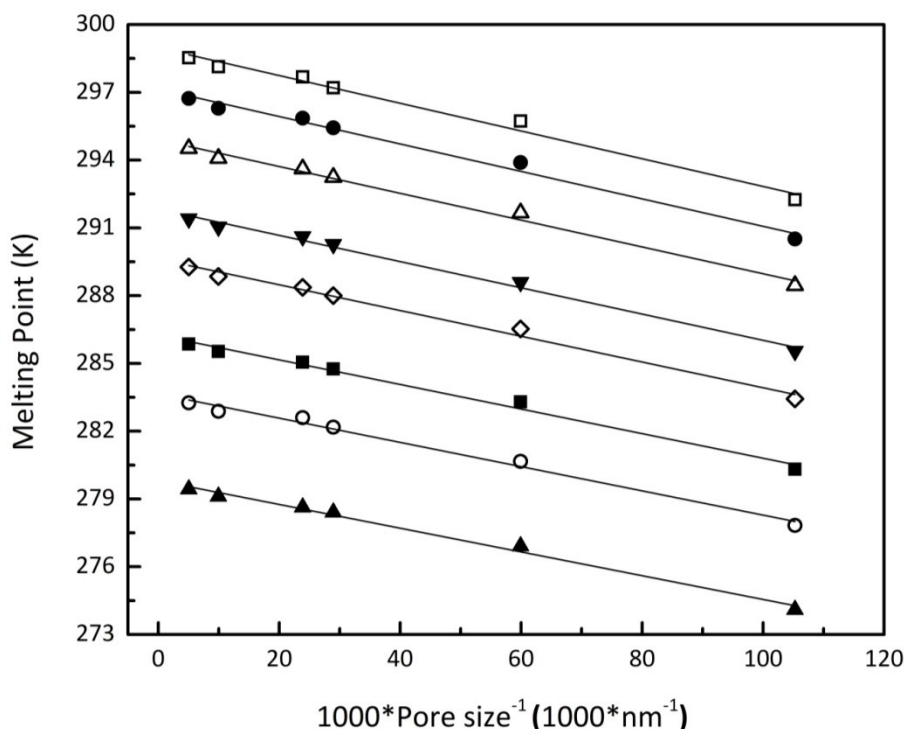


Figure 4.14 Melting point of methane hydrate versus reciprocal of pore sizes (Error bars are smaller than the symbols); □, 50 MPa; ●, 40 MPa; △, 30 MPa; ▼, 20 MPa; ◇, 15 MPa; ■, 10 MPa; ○, 7.5 MPa; ▲, 5 MPa.

Figure 4.14 shows the isobaric melting point of the pore hydrates versus the reciprocal of pore sizes: the linear behaviour is consistent with the Gibbs-Thomson equation expressed in terms of hydrate properties (see Eq. 4-1). The interfacial tension of methane hydrates in porous media was calculated by G-T equation from the isobaric melting points with different pore sizes. As indicated by the NMR analysis [159, 163] and calorimetry measurements [164, 165], an unfrozen water layer, which has a thickness around 0.4 nm, is present along the pore wall. The existence of a quasi-liquid layer on ice surfaces was also confirmed by AFM measurements [166]. Hence, a fully wetted contact angle of 0° was assumed along with a

constant density and melting enthalpy of hydrates to calculate the interfacial tension of methane hydrates within a porous material. By assuming the same density and enthalpy used by Anderson and coworkers (914 kg/m³ and 53.2 kJ/mol) [131], the calculated interfacial tension at low pressures was comparable with the value obtained by Uchida et al. [125] and Anderson et al. [131]. Based on their experimental data, Anderson et al. concluded that the interfacial tension of methane hydrates was 32 ± 3 mJ/m² over a pressure range of 3.6 MPa to 14.1 MPa [131]. In this work, the averaged interfacial tension of 5 MPa, 7.5 MPa, 10 MPa and 15 MPa from this study is 34.3 ± 1.9 mJ/m².

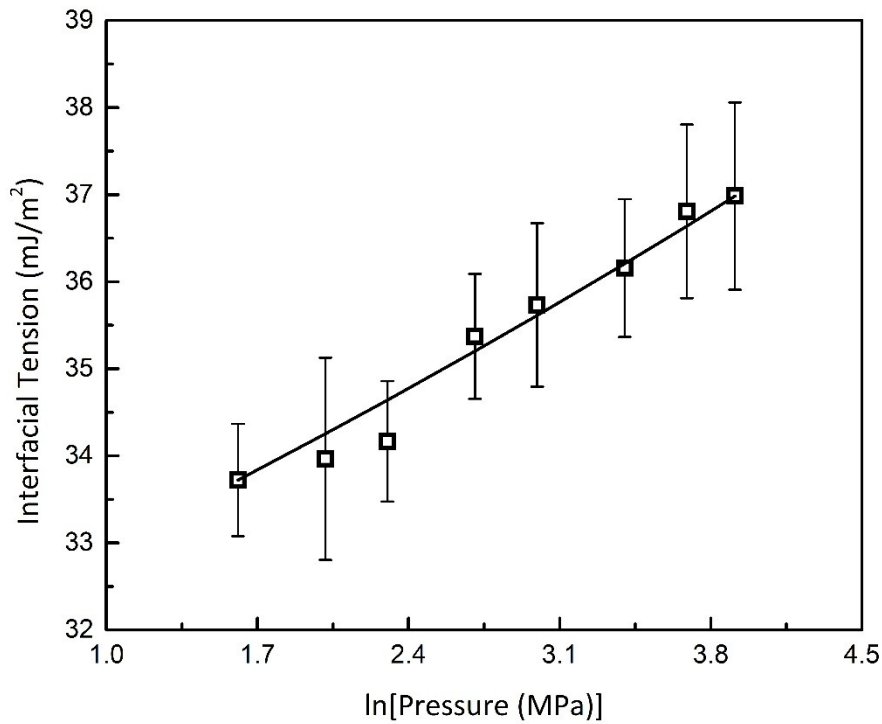


Figure 4.15 Interfacial tensions of methane hydrates in porous media (Error bars shows the uncertainty of the calculated interfacial tension, the solid line shows the estimated interfacial tension using Eq. 4-2)

As illustrated in Figure 4.15, the calculated interfacial tensions increase significantly with pressure in an approximately logarithmic manner. Therefore, an empirical parameter, β , was added into the Gibbs-Thomson equation as follows.

$$\frac{T_{mb} - T_{pore}}{T_{mb}} = \frac{2 \cdot \gamma}{\Delta H_{fus} \cdot \rho_{Hydrate} \cdot r_{pore}} \cdot \beta \quad (4-2)$$

The parameter, β , was used to include the pressure (P) effect on confined melting points using the function:

$$\beta = 1 / [a + b \cdot \ln(P / \text{MPa})] \quad (4-3)$$

where parameters a and b were fitted to the data presented in Figure 4.15. P is the system pressure. The fitted parameters and associated physical properties are summarised in Table 4-4

Table 4-4 Parameters and physical properties used in the modified G-T Equation, Eq. 4-2

Hydrate Density	kg/m ³	914
Hydrate Heat of Fusion	kJ/mol	53.2
Hydration ratio	-	6.0
Interfacial Tension at 5 MPa	mJ/m ²	33.72
a	-	1.002612
b	-	-0.031533

The empirical parameters were calculated with respect to the interfacial energy at a reference pressure of 5 MPa and assuming constant density and enthalpy of fusion. These latter thermophysical properties are difficult to measure in porous media. In the bulk phase, the density of hydrates could be estimated using the thermal expansion coefficient and compressibility [32]. The enthalpy of fusion is known to vary with pressure. However, the enthalpy data from this study and density data from Helgerud et al. [32] suggest that the pressure variation in bulk density and bulk enthalpy for solid hydrate is not strong. In the light of the difficulties in obtaining properties in porous media, the bulk density, the melting enthalpy in bulk and measured interfacial energy at 5 MPa were applied to the modified G-T equation, Eq. 4-2. The empirical parameter, β , was used to compensate for any pressure effects, most likely associated with interfacial tension. The modified G-T equation provides a semi-empirical equation to calculate the confined melting points under elevated pressures within the range 5-50 MPa and 274.1-298.5 K. The expanded uncertainty was estimated by

multiplying the standard uncertainty of the correlation with a converge factor that took account of the confidence interval. The expanded uncertainty of the correlation was estimated to be 0.20 K with a confidence interval of 95%.

4.8.6 Empirical Correlation

The Gibbs-Thomson equation predicts the melting temperature shifts from the bulk melting points. It requires a knowledge of methane hydrates' bulk melting points to predict the melting points in porous media. When the bulk properties are unknown, it is helpful to have an empirical equation to correlate pressures, confined melting points, and pore sizes. The following empirical equation is valid over a pressure range of 5 MPa to 50 MPa, and in a temperature range of 274.1 K to 298.5 K. All data from this study were used to fit one equation, containing in total 7 parameters, as follows:

$$T_{pore} / K = a_1 + a_2 \cdot (P / MPa) + \frac{a_3}{a_4 + (P / MPa)} + [a_5 + \frac{a_6}{(P / MPa)}] \cdot (R_{pore} / nm)^{-1} + a_7 \cdot \cos(R_{pore} / nm) \quad (4-4)$$

The parameters in Eq. 4-4 are given in Table 4-5. The expanded uncertainty of the empirical correlation was 0.11 K with a 95% confidence interval.

Table 4-5 Parameters in Eq. 4-4 for the correlation of the melting temperature of confined methane hydrates

a_1	294.738839
a_2	0.134310
a_3	-137.059913
a_4	3.752531
a_5	-48.159863
a_6	-0.186206
a_7	-0.116622

4.8.7 Uncertainties and Error Propagation

Standard uncertainties for experimental quantities are estimated by using practices suggested by Guide to the Expression of Uncertainty in Measurements (GUM) [167]. The overall relative standard uncertainty $u_{T,pore}$ was calculated from the following equation:

$$u_{T,pore}^2 = \left[\frac{\partial f(T)}{\partial R} u_P \right]^2 + \left[\frac{\partial f(T)}{\partial P} u_R \right]^2 + (u_T)^2 \quad (4-5)$$

where u_X donates the relative standard uncertainty of variable X (i.e., P , R , and T). $f(T)$ is Eq. 4-2 which correlates the confined melting points with pore size and pressure. The estimated uncertainty of pressure (u_P), pore size (u_R) and temperature (u_T) are 0.046 K, 0.0001 K and 0.080 K, respectively. The calculated overall uncertainty $u_{T,pore}$ is ± 0.184 K.

4.8.8 Impact of Surface Chemistry

As suggested by the Gibbs-Thomson equation, interfacial energy is one of the key parameters that affect the phase equilibrium in porous media. However, a limited amount of literature data were found to quantify the impact of interfacial energy in porous media on the phase equilibrium of confined methane hydrates. It is partially due to the fact that quantifying the surface chemistry inside the porous media, especially in mesoporous and microporous media, is strenuous. A semi-quantitative analysis of the effect of surface chemistry in porous media was conducted by grafting Vycor 8 and Vycor 40 samples with hydrophobic and hydrophilic groups.

Grafting porous silica was achieved by exposing porous silica materials with functional salines as detailed in section 4.7.6. The phase behaviour of methane hydrates in Vycor 40, hydrophobic Vycor 40 and mesoporous carbon was tested at 20 MPa (see Figure 4.16).

The melting points of hydrophobic Vycor 40 and mesoporous carbons are 291.59 K and 291.61 K, respectively. Regardless of their small but different pore sizes (methylated Vycor 40 (40.3 nm) and mesoporous carbon (10 nm)), the melting points in hydrophobic porous media were comparable with the melting point of bulk hydrates (291.47 K) at 20 MPa, suggesting that hydrophobic surfaces eliminated the confinement effects caused by small pores. However, it was also possible that water was retained outside the porous network. Hence, a bulk behaviour was observed.

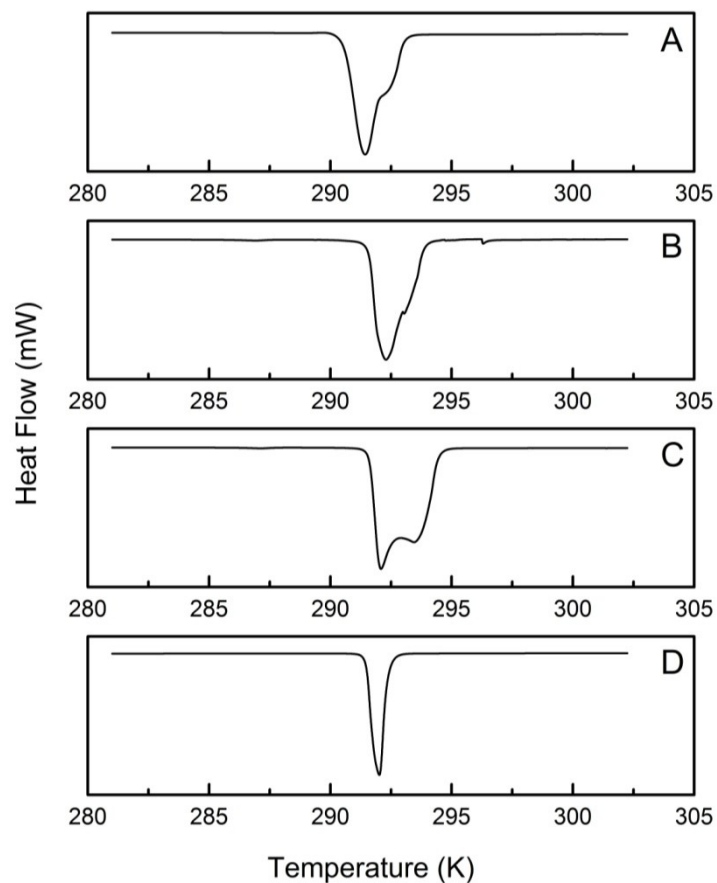


Figure 4.16 Decomposition of methane hydrates in different media at 20 MPa: A, Vycor 40; B, hydrophobic Vycor 40; C, Mesoporous carbon; D, bulk hydrates

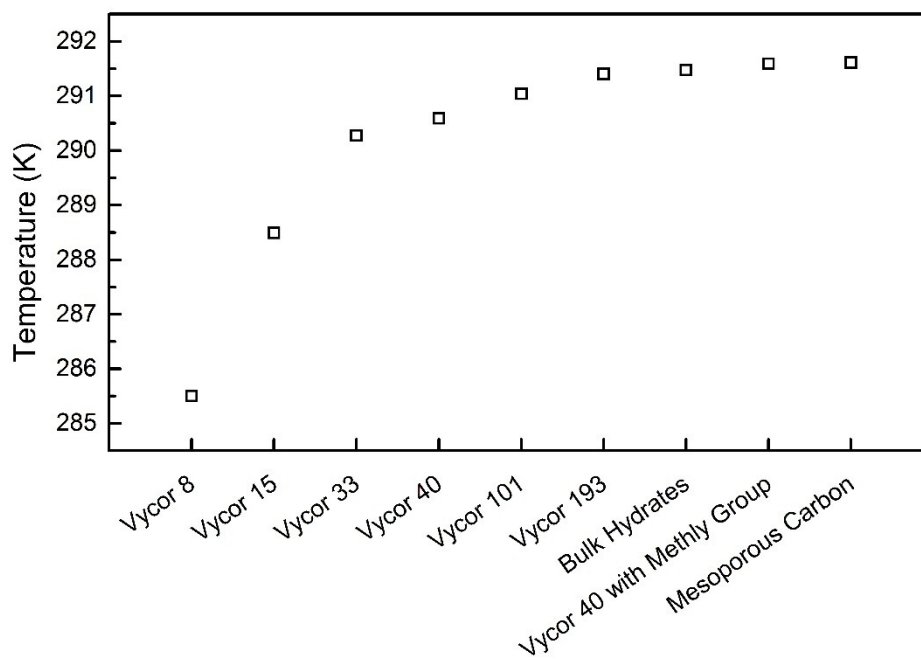


Figure 4.17 Melting points of methane hydrates in bulk, untreated Vycor samples and hydrophobic media at 20 MPa

During the grafting process of porous silica in aqueous systems, large pores were preferred due to the accessibility of the internal pore surfaces. However, the confinement effect of methane hydrates on melting points in Vycor 40 was not as profound as small pores (see Figure 4.17). Vycor 8 samples were used for the subsequent tests due to large confinement effects. Results are summarised in Figure 4.18 and Table 4-6.

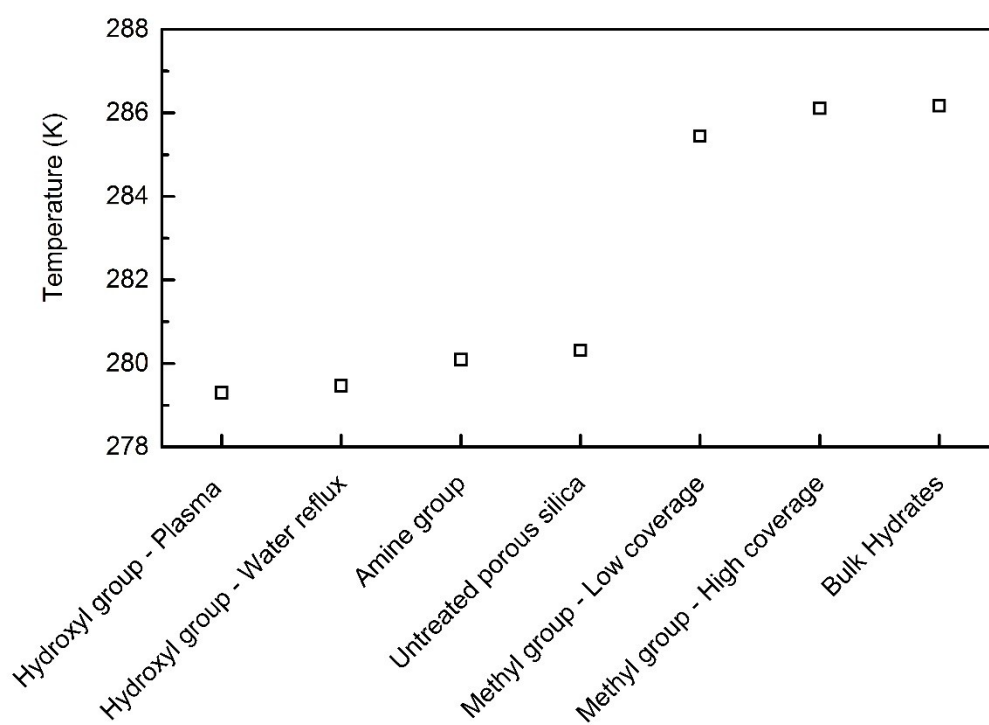


Figure 4.18 Melting points of methane hydrates in bulk, untreated Vycor 8, hydrophobic Vycor 8 and hydrophilic Vycor 8 at 10 MPa

Table 4-6 Melting points of methane hydrates in Vycor 8 samples with different pore surface chemistry at 10 MPa

Types of Porous Media	Melting Point of Hydrates / K
Hydroxyl Group (Plasma)	279.30
Hydroxyl Group (H ₂ O Reflux)	279.47
Amine Group	280.09
Untreated Porous Silica	280.32
Methyl Group 1 Low Coverage	285.45
Methyl Group 2 High Coverage	286.11
Bulk Hydrates	286.17

At 10 MPa, the melting points of methane hydrates in hydrophilically treated Vycor 8 were lower than in untreated Vycor 8 by up to 1 K. The plasma treated silica particles showed the most pronounced reduction of the melting point. Amine groups and hydroxyl groups from water reflux had a minor promotion of the confinement effect (depression of the melting points). The confinement effect in two methylated Vycor 8 samples was reduced and melting points of methane hydrates in hydrophobic porous media again showed similar melting points as bulk hydrates.

The results indicate that the surface chemistry of the porous medium plays a significant role in determining the melting point of methane hydrates confined within its pores. The more hydrophilic the pore surface, the greater the depression of the pore hydrate melting point, indicating strong interaction between the hydrogen-bonding cage structure and the hydrophilic surface groups capable of similar polar or hydrogen bonded interactions. By contrast, hydrates formed in pores with hydrophobic surface chemistries (even of low diameter) melt at essentially the same temperature as bulk gas hydrates, indicating negligible interaction of the hydrate structure with the non-polar surface. The difference observed here between highly hydrophilic and hydrophobic surfaces was up to 7K. Reservoir rocks can vary greatly in their wetting characteristics, or hydrophilicity, so such effects could be really significant for natural hydrates confined in reservoirs or sediments of different mineralogies or ageing environments.

4.9 Summary

Hydrate phase equilibria of binary methane and water mixtures were measured by a high-pressure differential scanning micro-calorimetry in mesoporous and macroporous silica that have controlled pore size ranging from 8.5 nm to 195.7 nm. An oscillating dynamic method was used to form hydrates and the equilibrium temperatures of gas hydrates were determined calorimetrically. In porous media, depressed melting points of methane hydrates were observed and the confinement effect was more pronounced with small pores. The confinement effect was fitted by a modified Gibbs-Thomson equation, in which an empirical parameter was used to compensate the observed pressure dependency of the Gibbs-Thomson slope.

The effects of interfacial energy on phase equilibria were investigated by using functionalised porous silica. The confinement effect is promoted by hydrophilic surfaces and inhibited by hydrophobic surfaces. Methane hydrates in porous hydrophobic silica tended to behave as bulk methane hydrates in terms of the equilibrium temperature.

Other properties including enthalpy of fusion, formation and decomposition kinetics in a static system were also experimentally measured. The enthalpy of hydrate fusion of methane hydrates showed a minor pressure dependency and increased 1.8 % from 5 to 40 MPa. Under the tested conditions, hydrate formation in porous media were promoted at 10 MPa and 20 MPa due to the excess interfacial area. Self-preservation effect were observed when gas hydrates formed and melted at different pressures.

The measured phase equilibria data, enthalpy of fusion, and impact of interfacial energy were considered as relevant parameters for gas hydrate simulation models. The proposed models could be used to predict phase behaviour of gas hydrates in confined media.

Chapter 5

Reactor Design for *in-situ* Hydrate Measurements

5.1 Introduction

This chapter describes a unique optical cell suitable for (Raman) spectroscopic studies of a wide range of multiphase systems under controlled pressure and temperature conditions. The design was motivated by the objective to use Raman spectroscopy to study gas exchange processes in methane hydrate systems.

Raman spectroscopy provides a powerful means of understanding multiphase materials at a molecular level. This technique interrogates the fundamental vibrations of the assembly of molecules that make up a material. In the case of gas hydrates, it can distinguish collective lattice vibrations of the clathrate water cages from the guest gas molecule vibrations and the intramolecular vibrations of individual water molecules. Several authors have used Raman spectroscopy to study gas hydrates, either by off-line synthesis methods or via *in situ* point measurement [168-170]. In off-line measurements, gas hydrates were formed in a separate reactor and quenched into liquid nitrogen before being introduced into the spectrometer. The Raman spectra were generally obtained at ambient pressure although some experiments were performed at elevated pressures [171]. The Resolution of confocal and widefield systems is governed by diffraction limits. However, confocal systems reject out-of-focus signals and provide a higher resolution than non-confocal (widefield) systems. Most studies used a single point measurement method, where the laser light source was focused by a confocal or widefield optical system. The Raman spectra were taken at a single point in the sample, which was assumed to be representative of the entire sample. However, the incorporation of guest gas molecules into hydrate structures is not necessarily uniform, and the interest of this work is in studying the spatial heterogeneities of the molecular composition in such materials by

using real-time *in situ* 3D Raman imaging as a function of temperature and pressure across the phase diagram.

To use confocal Raman spectroscopy with a translation stage to study gas hydrates under extreme conditions of temperature and pressure, therefore, a new optical high-pressure cell was designed and commissioned. The cell has been designed to meet the following requirements: (i) it should be capable of working at pressures to 50 MPa and at temperatures from 288 to 353 K; (ii) it should provide stable temperature control (± 0.020 K) and rapid temperature response (Up to $5 \text{ K}\cdot\text{min}^{-1}$); (iii) it should have an optical window for Raman measurements; (iv) it should have the capability to measure sample temperature and pressure accurately; and (v) the dimensions of the cell should be compatible with a Leica confocal microscope (Model DM2500 M). Such a cell is of course suitable for Raman spectroscopy and imaging of a wide range of materials and multiphase systems under extreme conditions. This chapter presents details of its design, construction and operation, illustrating its capabilities with some typical results, before applying it to study gas hydrate exchange reactions in detail in Chapter 6.

5.2 Reactor Design

5.2.1 Main Body of the Cell

Three-dimensional Raman Imaging was achieved by the combination of a confocal Raman microscope, a motorised stage (resolution $0.1 \text{ }\mu\text{m}$) and a high-pressure cell with precisely controlled temperature that confines the sample. The cell design was most constrained by the available space for the height of the cell, which was limited by the optical system of the commercial Raman microscope, in this case a Leica confocal microscope (Model DM2500 M). In order to fit the reactor between the bottom of the objective and the top of the translation stage, the fluid connections and the temperature control system needed to spread out in the horizontal direction. The cell itself (see Figure 5.1) was composed of a block (F) of 17-4 PH martensitic precipitation-hardened stainless steel, with a top sight window and four side ports. 17-4 PH steel was selected due to its high mechanical strength and good corrosion

resistance. A plate face geometry was used to seal the pressure cell with eight high tensile screws (A) (M4 x 0.7, Grade 10.9 with the minimal tensile strength of 1000 MPa, Cromwell Tools Ltd). The dimensions of the Teflon gasket (D) (Virgin Grade PTFE, Gilbert Curry Industrial Plastics Co. Ltd.) was machined to match closely the internal diameter of the top lid (16 mm) and the outer diameter (10 mm) of the sapphire window (C). The height of the Teflon gasket was 5.5 mm, which was larger than the available void space of the top lid (5 mm). When the gasket was compressed during installation by the top plate (B), the excess material in the vertical direction was deformed and translated in the horizontal direction into close contact with the $0.3 \text{ mm} \times 45^\circ$ chamfered side faces of the sapphire window (C), thereby sealing this window into the cell. This seal could be re-used to a limited extent; typically a change after seven opening-closing cycles of the cell is necessary.

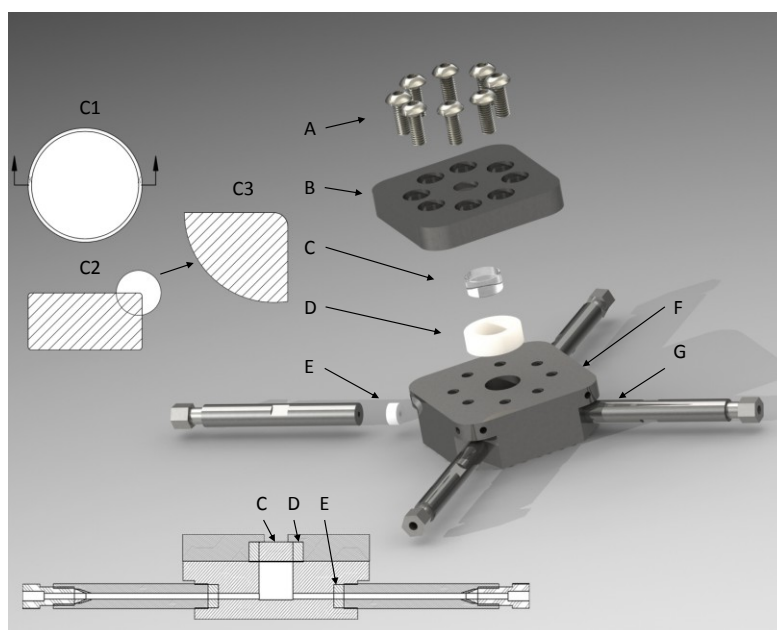


Figure 5.1 Exploded view of the cell main body (A: High tensile screws B: Top lid C: Sapphire window C1 Top view of sapphire window C2: Cross section view of sapphire window C3 Expanded view of sapphire window D: Large Teflon gasket E: Small Teflon gasket F: Vessel base G: 1/4" Valco tube adapter).

Two side ports permit connections of the temperature probes, and two are used as gas/liquid inlets and outlets (G). 1/16" Valco fittings were chosen to connect the high-pressure fluid inlets and outlets due to their small cross-sections. 1/4" tube adapters with a high pressure 1/16" fitting at end side were supplied by Valco Instruments (part number ZTA41). The blank sides of the tube adapters were threaded with M6 x 1 threads and sealed to the reactor with a

small Teflon gasket E (O.D. 6 mm, I.D. 1.5 mm). Two temperature measurement ports and one liquid inlet port are connected to the bottom of the reactor (see Figure 5.2). One of the gas inlet/outlet port was channeled with an angle of 125° to enable gas inlets and outlets at the top of the cell. Two fast response platinum resistance thermometer (PRT) probes with a time constant of 1.5 s were supplied by Fluke (Fluke 5612). Two Vespel adapters sealed the 1 mm O.D. temperature probes to the 1/4" tube adapters.

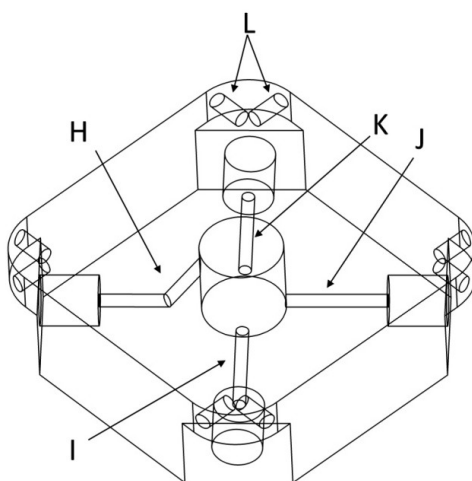


Figure 5.2 Wire sketch showing the internal channel arrangement of the vessel base (H: Top inlet/outlet, I: Bottom inlet/ outlet, K and J: Temperature probe ports, L: M2 holes for clamping copper block).

A few sterling silver inserts (see Figure 5.3) of cylindrical shape (9.8 mm in diameter) with different heights, were made to adjust the cell volume and height. Sterling silver was selected due to its high thermal conductivity. Two side grooves (see Figure 5.3B) facilitated the process of introducing and removing gases. Two bottom grooves (see Figure 5.3A) contacted with the temperature probes. Thermal contacts were improved by using silicone based thermal paste (thermal conductivity $5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) supplied by RS Components (Part number 7074736).

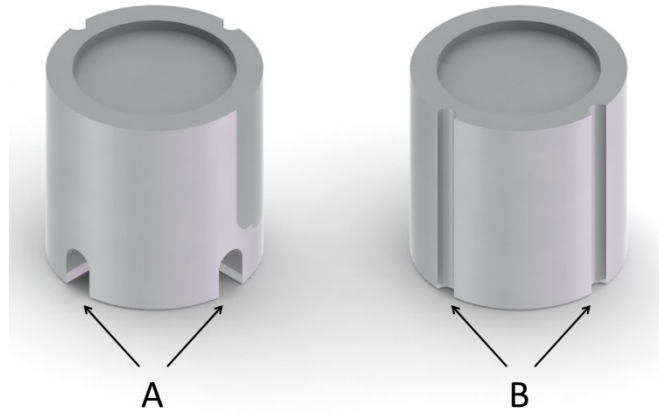


Figure 5.3 Geometry of silver inserts A) Bottom groove for temperature probes; B) Side groove for gas inlet and outlet.

5.2.2 Pressure Vessel Design

The dimensions of the high-pressure optical cell were determined by adopting the practices suggested by the High-Pressure Technology Association [172]. A design safety factor of 4 was used for all calculations. Both yield strength (0.2 % offset*) and ultimate tensile strength of the materials were used [173]. Material properties and calculation results are summarised in Appendices C and D.

It is worth noting that the screws in the reactor (see Figure 5.1A) were not fully engaged due to the thickness of the top lid. Standard tensile areas of screws are not valid in this scenario. A selection guide published by Brickford and Nassar [174] was used to determine the minimal length of engagement for screws. A general material rule for screws is that the material strength for the internal threads (in this case the main body of the cell) should be larger than that of external threads (i.e., the screws). The material strength of the main body material (17-4 PH stainless steel) and the screws (Grade 10.9 stainless steel) fulfilled this criterion.

When the reactor was under pressure, the following equation can be written.

$$n \cdot A_s \cdot \sigma \geq A_p \cdot P_{sys} \quad (5-1)$$

* 0.2 % offset yield strength is defined as a stress required to produce a non-proportional elongation of 0.2 % [173].

where n is the number of screws; A_S is the thread shear area (mm^2); σ is the material tensile strength ($\text{N}\cdot\text{mm}^{-2}$); A_P is the area exposed to pressure (mm^2); P_{sys} is the system maximum working pressure ($\text{N}\cdot\text{mm}^{-2}$). The minimal length of engagement could be estimated by the following equation.

$$LE = \frac{A_S \cdot p}{\pi \cdot D_{1\max} \cdot [p / 2 + 0.57735 \cdot (d_{2\min} - D_{1\max})]} \quad (5-2)$$

where LE is the minimal length of engagement (mm); A_S is the thread shear area; p is the pitch (mm); $D_{1\max}$ is the maximum diameter of internal thread (mm); $d_{2\min}$ is the minimum pitch diameter of external thread (mm). The minimal length of engagement can be estimated by combining Eq. 5-1 with Eq. 5-2.

Finite element analysis (FEA) is a useful analysis tool and suitable for many engineering applications including stress analysis, thermal analysis, vibration analysis etc. Its main advantages stem from the ability to be applied to arbitrary shapes in any number of dimensions. Here, FEA stress analysis was used to evaluate the stress load on core parts of the cell (see Figure 5.4, and Figure 5.5). The analysis was carried out based on calculating von Mises stress (effective stress) under static stress load. Triangular meshes with a nominal size of 0.4 mm were used. The mesh size was determined by stepwise reducing the mesh size until no obvious changes in the calculated results were observed. von Mises stress is a failure criterion based on distortional strain energy. It is applicable for ductile materials and is compared to the yield stress (0.2 % offset) of the materials; a material starts to yield when the von Mises stress reaches the yield stress of the material [175].

In the stress analysis performed for the cell, local high-stress points were identified. The calculated von Mises stresses were within 50% of the yield stress. High-stress load was observed on the contact surface of the sapphire window. It was also found that sapphire windows without chamfers experienced high-stress load on the sharp edges.

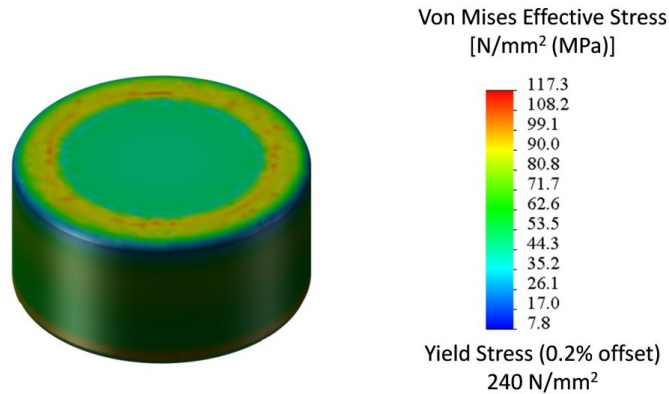


Figure 5.4 Stress analysis of the sapphire window.

The number and the length of the screws were determined by the effective tensile area which was based on the contact area of the threads. High-stress loads could always be avoided by using longer screws. However, excessive lengths that are practically difficult to use should be avoided. It was also important to check that the neck of the screw could withstand the stress under maximum working pressure (see Figure 5.5). The stress was loaded at the bottom of the socket screws and the threads at the end were fixed (as indicated by the yellow arrows). The maximum von Mises stress was detected around the neck of the screw. Originally, Torx type screws were considered due to larger contact areas and their resistance to stripping. However, commercially available Torx type screws were only available with medium tensile stress grades with a yield strength (0.2 % offset) up to 600 MPa. Socket head screws were used in the end due to their high yield strength (0.2 % offset) of 940 MPa.

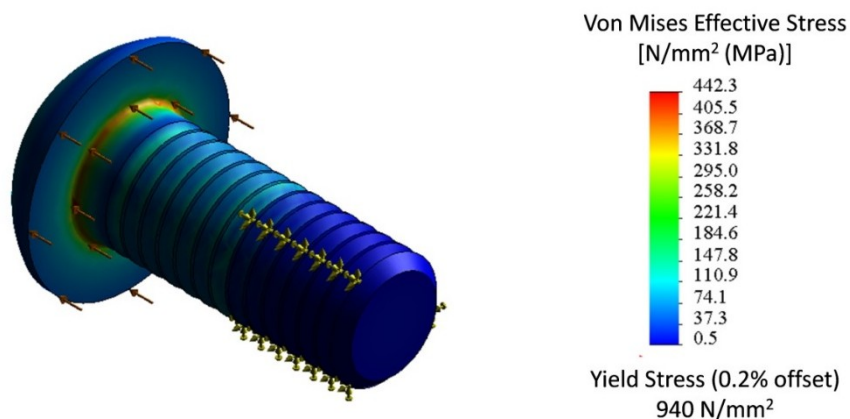


Figure 5.5 Stress analysis of the socket head screw. Red arrows show the direction of force load and yellow arrows indicate fixed (clamped) locations.

5.2.3 Temperature Control and Insulation

A particular challenge for precision studies is the accurate and uniform control of the temperature of the cell block and of the sample chamber. The temperature of the cell was regulated by using four single-stage Peltier elements (21.2 W each, RS Component, 4901339) attached to the side of the reactor (see Figure 5.6). A group of two Peltier elements was connected in series, and the two groups were connected in parallel. The Peltier modules could heat or cool the reactor depending on the polarity of the current supplied to the module.

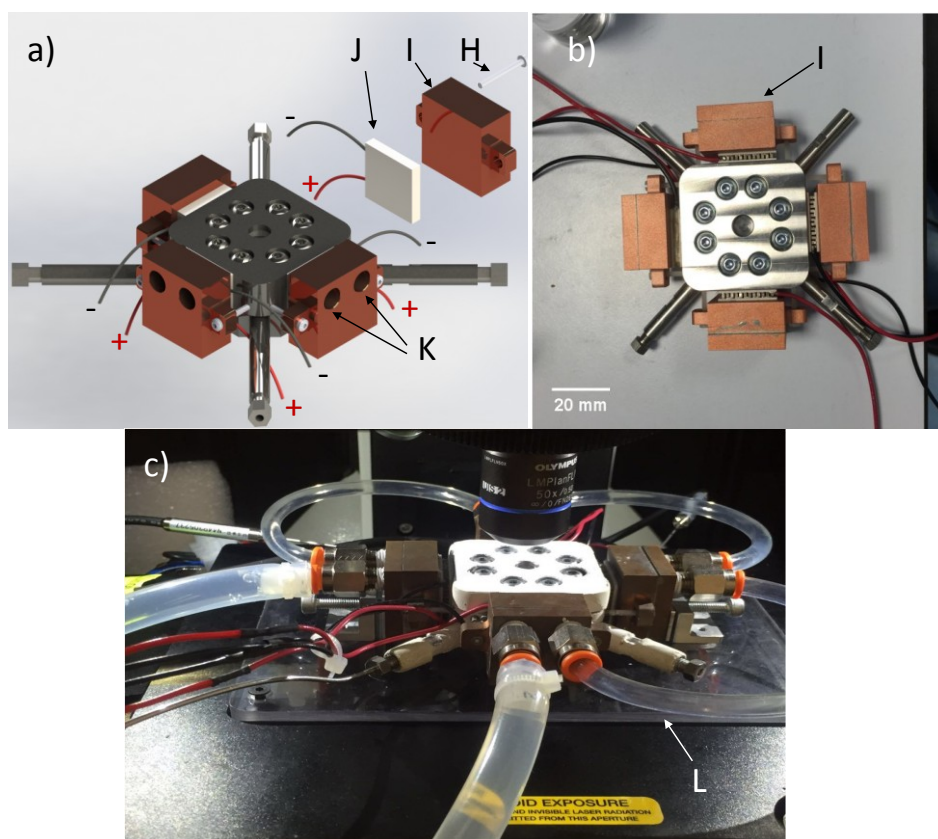


Figure 5.6 a) Geometry of Peltier element cooling array b) Assembled high-pressure optical cell, c) Insulated high-pressure cell fitted between translation stage and objective. (H: M2 screws for clamping copper blocks and Peltier elements, I: Vacuum brazed copper block with internal flowing channels. J: Peltier element, K: 1/16" Push-in connectors on copper blocks, and L: 1/4" Polyurethane tubing).

A bipolar H-bridge temperature controller (Electron Dynamics UK, TCM PCB) was used to regulate temperature and interfaced by a USB cable to the supplied computer control software. The temperature controller generated Pulsed Width Modulation (PWM) signals by utilising

four metal oxide semiconductor field effect transistors (MOSFETs). When the Peltier units were driven by the PWM inputs, the Peltier effect occurred with the Joule effect, resulting in heating and reducing the efficiency of the Peltier elements [176]. These side effects of the PWM temperature controller were overcome by using high-power Peltier units and efficient copper blocks for dissipating the heat. Alternatively, a direct current Peltier controller could be used to improve the efficiency of the Peltier elements. It is also worth noting that commercial Peltier elements have ceramic surfaces attached to both sides. The efficiency of the Peltier elements could be further improved by using metallic surfaces on the elements.

Excess heat from the hot side of the Peltier elements was dissipated by four vacuum brazed copper blocks (see Figure 5.7) through which was circulated water controlled at 283 K from a thermostat bath. The internal multi-channel structure greatly increased the surface area and hence improved the efficiency of the heat removal process.

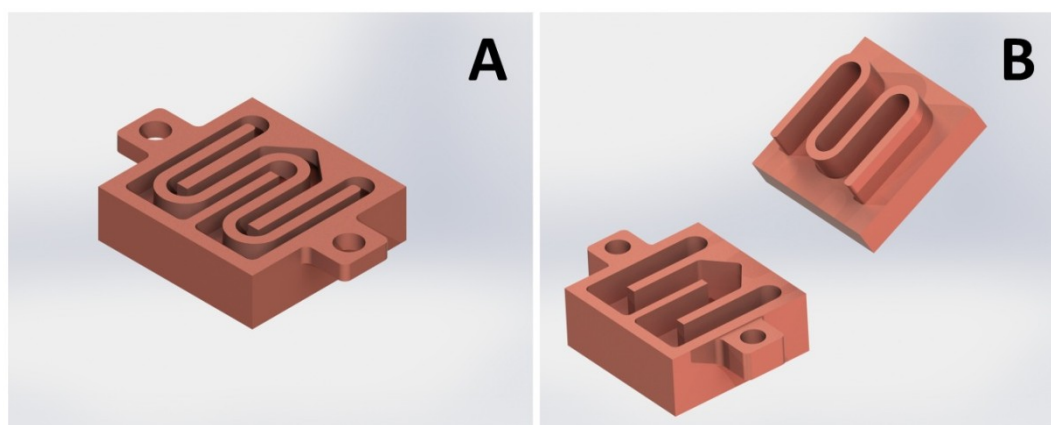


Figure 5.7 Internal structure of copper blocks, A) cross-section view of the internal structure; B) Base and lid of the copper block.

The copper block could be plated with a thin anti-corrosion surface, which might be favourable for some harsh environments. Here, the copper blocks were used without any plating to minimise potential reduction in thermal conductivities. In order to further enhance the heat transfer between the Peltier's ceramic surface and the metal surfaces, silicon-based, deformable heat conductive pads (RS Component, 7074714) were used to eliminate the macro void spaces between different surfaces. (Carbon-based pads were found to be inferior due to

their limited deformability). The Peltier elements and thermal blocks were clamped to the main cell body by $M2 \times 0.4$ screws.

To provide good thermal insulation, the cell was spray coated with Aerogel (Aerocoat 120, Aerogel UK Ltd). This porous silica-based coating had a very low thermal conductivity of $0.009 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and effectively eliminated conductive heat losses.

In case of a failure in dissipating heat from the Peltiers (i.e., losing the circulated water), the power supplied to the Peltier elements would be accumulated, leading to over-heating of the system. A safety limit of 383 K was implemented in the control software and an extra safety cut-out controller was also added between the Peltiers and their power supply. When the temperature of a type T thermocouple in contact with the cell exceeded 383 K, the safety controller would cut out the power to the Peltier elements. An in-line thermal switch with a fixed cut-out temperature could also be used as a simple alternative approach.

5.3 High-pressure Raman Apparatus

The high-pressure Raman apparatus (shown schematically in Figure 5.8) consisted of the Raman optical cell, temperature and pressure sensors, and a high-pressure pump (Teledyne Isco, model 260D, Teledyne Technologies Inc.). The high-pressure cell was placed inside the Raman optical enclosure. In order to avoid condensation on the reactor, especially on the optical window, nitrogen gas was continuously injected into the enclosure. Additionally, a separate Peltier element cooled a metal block to 256 K, which absorbed residual moistures in the enclosure. No condensation was observed when the cell operated at 248 K for several hours.

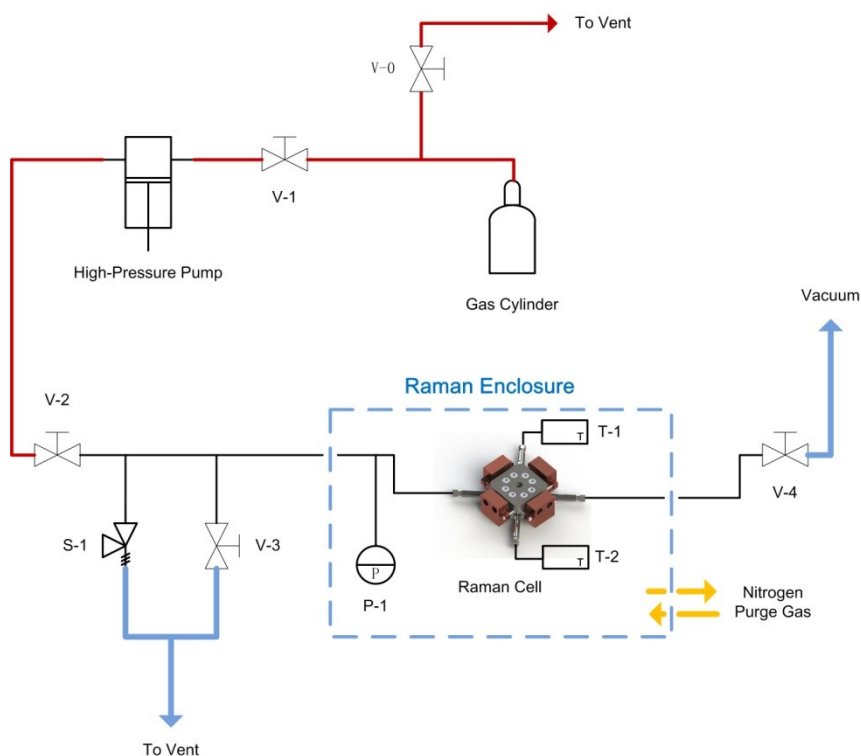


Figure 5.8 Schematic diagram of the Raman apparatus. V-0, V-1: High-pressure Venting Valve, V-1, V-2: High-pressure pump isolation valve, V-4: High-pressure valve for vacuum line, S-1: Safety Head, P-1: Pressure sensor, T-1, T-2: Platinum-resistant temperature sensors. — 1/16" High-pressure tubing, 1/8" High-pressure tubing — 1/4" PTFE tubing, — Nitrogen Purge gas.

5.3.1 Calibration of temperature and pressure

The two PRT probes (5622 Fluke UK) were calibrated against a standard platinum resistance thermometer with an expanded uncertainty of 2 mK over a temperature range of 243 K to 353 K according to the ITS-90 scale [177]. The triple point of water (TPW) was realised by immersing a triple point water cell (Fluke, 5901) in a TPW maintenance apparatus (Fluke, 9210). The uncertainty of the TPW was better than 0.1 mK.

The International Temperature Scale of 1990 (ITS-90) was accepted by the International Committee of Weights and Measures at a meeting in 1989. ITS-90 has a few advantages over other temperature scales or calibration methods. Fixed temperature points are easier to realise and measured to a high degree of accuracy. Temperatures are calculated by comparing the difference of a PRT's resistance at different temperatures and its resistance at the Triple Point of Water (TWP). There are a few sub-regions in ITS-90 that cover different temperature

ranges. In this work, sub-region 4 (13.8033K to 273.16K) and sub-region 8 (273.16K to 1234.93K) were used for the calibrated temperature probes.

Temperatures were determined by the ratio of the resistance $R(T_{90})$ at temperatures of fixed points (T_{90}) and the resistance $R(273.16K)$ at the triple point of water. The ratio ($W(T_{90})$) is defined as:

$$W(T_{90}) = \frac{R(T_{90})}{R(273.16K)} \quad (5-3)$$

At each fixed point, T_{90} (temperature) and $W_r(T_{90})$ (reference resistance) are correlated with a reference function or an inverse function, defined as part of ITS-90 in the temperature range of 13.8033K to 273.16K.

$$\ln[W_r(T_{90})] = A_0 + \sum_{i=1}^{12} A_i \left[\frac{\ln(T_{90}/273.16K) + 1.5}{1.5} \right]^i \quad (5-4)$$

An inverse function, which is equivalent to Eq. 5-4 to within 0.1 mK, is defined as:

$$T_{90}/273.16K = B_0 + \sum_{i=1}^{15} B_i \left[\frac{W_r(T_{90})^{1/6} - 0.65}{0.35} \right]^i \quad (5-5)$$

For a temperature range of 273.16K to 1234.94K, the following reference function is defined.

$$W_r(T_{90}) = C_0 + \sum_{i=1}^9 C_i \left[\frac{T_{90} / K - 754.15}{481} \right]^i \quad (5-6)$$

An inverse function, which is equivalent to Eq. 5-6 to within 0.13 mK, is defined as:

$$T_{90}/K - 273.15 = D_0 + \sum_{i=1}^9 D_i \left[\frac{W_r(T_{90}) - 2.64}{1.64} \right]^i \quad (5-7)$$

The values of the constants A_0 , A_i , B_0 , B_i , C_0 , C_i , D_0 and D_i are calculated by fitting the calibration data.

When temperatures are not at the predefined fixed point, deviation functions are used to adjust the resistance. Parameters of the deviation function are obtained from calibration data. The deviation function adjusts $W_r(T_{90})$ through the following equation.

$$W_r(T_{90}) = W(T_{90}) - \Delta W(T_{90}) \quad (5-8)$$

where $W_r(T_{90})$ is the new reference resistance. $W(T_{90})$ is the resistance ratio from Eq. 5-3 and $\Delta W(T_{90})$ is the deviated resistance obtained from Eq. 5-9 (sub-region 4) and Eq. 5-10 (sub-region 8).

$$\Delta W(T_{90}) = W(T_{90}) - W_r(T_{90}) = a_4 [W(T_{90}) - 1] + b_4 [W(T_{90}) - 1] \cdot \ln W(T_{90}) \quad (5-9)$$

$$\Delta W(T_{90}) = W(T_{90}) - W_r(T_{90}) = a_8 [W(T_{90}) - 1] + b_8 [W(T_{90}) - 1]^2 \quad (5-10)$$

Taking into account the long term drift and fluctuations of the calibration bath, the PRT temperature measurement uncertainty was 30 mK with a confidence level of 95%. A pressure transducer (Keller UK, PX-33), with a full range of 50 MPa and a standard uncertainty of 0.1 % full scale, was connected to the gas inlet port.

The PID parameters within the Electron Dynamics control software were autotuned at 278 K. At a given temperature set point, the cell temperature could be stabilised to ± 20 mK. Reduced fluctuations of steady state temperatures were observed around the tuning temperature, 278 K.

5.3.2 Raman system

The Raman spectroscopy system consisted of a Renishaw inVia system based on a Leica confocal microscope system (model DM2500 M), fitted with a high-speed motorised stage and three monochromatic laser sources at 532nm, 785nm, and 830nm. All measurements were made in confocal mode in 180° backscattering mode. A 20× (0.4 N.A.) objective and 532 nm laser source provided a theoretical spot size of 1.44 μm , rising to 2.25 μm at 830 nm. Backscattered signals were dispersed by a diffractive grating with 2400 grooves/mm. The

Raman signal was recorded by a Peltier-cooled charged device (CCD) at 253 K. An edge filter provided a Stokes Raman scattering signal in a range 50 to 5400 cm^{-1} .

5.4 Demonstration of cell performance

5.4.1 Temperature Control Test

The maximum system cooling rate is governed by the insulation, the number of Peltier stages, and the temperature of circulated water through thermal blocks. With temperature of the circulated water at 283 K, cooling/ heating rates can be achieved between 0.05 $\text{K}\cdot\text{min}^{-1}$ to 2 $\text{K}\cdot\text{min}^{-1}$.

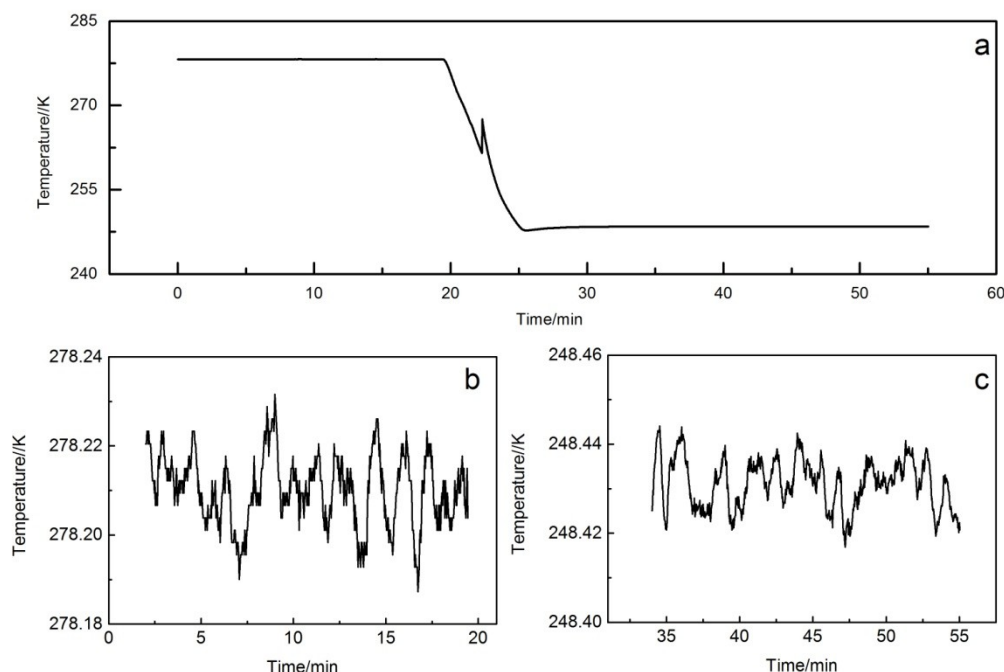


Figure 5.9 Temperature profiles of a fast cooling temperature test a) Temperature profile during a fast cooling rate ($5 \text{ K}\cdot\text{min}^{-1}$) from 278 K to 248 K with 0.3ml water in the cell b) Temperature stability during isothermal holding at 278 K, c) Temperature stability during isothermal holding at 248 K.

Higher cooling/heating rates up to $5 \text{ K}\cdot\text{min}^{-1}$ can be achieved (as shown in Figure 5.9), but with a significant temperature overshoot of around 0.7 K. Figure 5.9(a) illustrates the temperature profile of such a fast cooling test. 0.5 ml water sample was loaded into the cell, and the cell ramped at $5 \text{ K}\cdot\text{min}^{-1}$ between two isothermal holding regions at 278 K and 248 K.

A temperature spike at 22 min was observed due to the nucleation of ice at 261.5 K. The fast response temperature probe was able to detect nucleation events of a bulk solution. Figure 5.9b and Figure 5.9c show the temperature stability of ± 20 mK at different set points. The ice sample was then heated from 248 K to 283 K with a ramping rate of $0.06 \text{ K} \cdot \text{min}^{-1}$. *In-situ* Raman measurements were obtained 50 microns below the surface of the ice during the melting process. Raman intensities of ice peaks at 3142 cm^{-1} , which is the intermolecular hydrogen-bonded OH vibration of water molecules, were used to indicate the phase transition (see Figure 5.10). Raman spectra of ice (Figure 5.10A) and water (Figure 5.10F) showed different peak shapes (molecular interactions) and intensities (transparency). The onset point of high Raman intensity, Point C, corresponded to a cell temperature of $273.17 \text{ K} \pm 0.03 \text{ K}$. Other phase transition and phase equilibrium studies are also possible by utilising the temperature control system and Raman measurements.

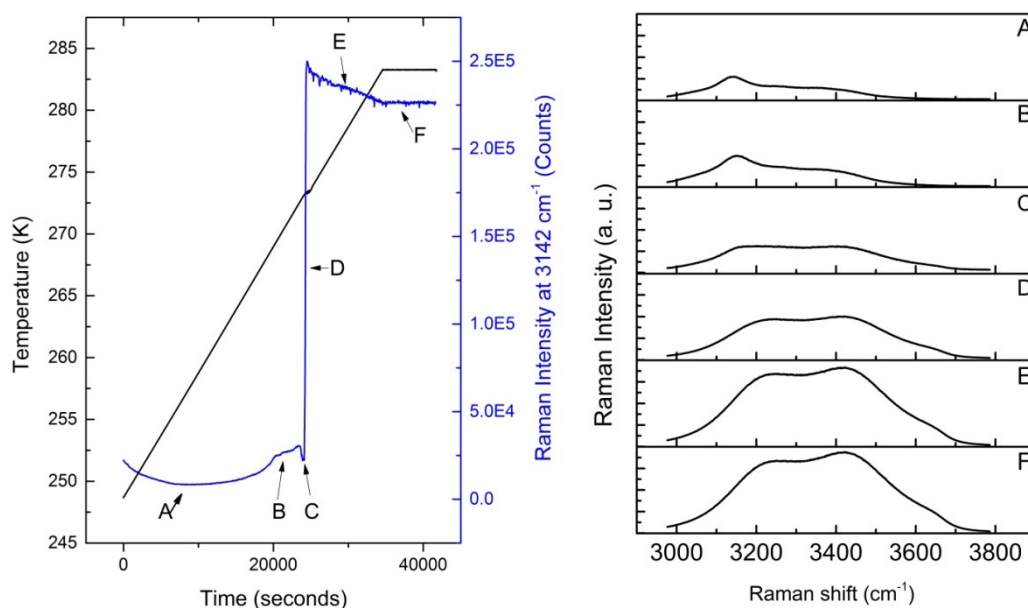


Figure 5.10 Ice melting at a heating rate of $0.06 \text{ K} \cdot \text{min}^{-1}$ with continuous Raman measurements (left), and Raman spectra of ice during the melting experiment (Right).

5.4.2 *In situ* Formation of Gas Hydrate Particles

In the absence of agitation, synthesising gas hydrates requires very long periods of time; especially when hydrate layers are formed at the gas-liquid interface, mass transfer can be very slow. A temperature oscillating method was used to achieve high hydrate conversion

with a short period of time [71]. 0.1 μL to 0.5 μL of deionised water was loaded into the bottom of the cell, followed by pressurising the cell to 20 MPa with methane gas (Research Grade, 99.995 purity BOC). The cell temperature was then cycled between 278 K and 253 K at a rate of 2 K $\cdot\text{min}^{-1}$. The majority of the water sample was converted into methane hydrate within 10 hours, as confirmed by Raman images.

5.4.3 Raman Spectra of Hydrates

Raman spectroscopy detects peaks at frequencies corresponding to the various intramolecular and collective vibrational modes of the different molecules in the sample. Fundamental vibrational frequencies correspond to the transition from the ground state (ν_0) to a higher energy state (ν_1). Overtone bands are observed when a molecule is excited from the ground state (ν_0) to an even higher energy state directly (ν_2 or ν_3), for example a first overtone ($2\nu_2$) is the transition from ν_0 or ν_2 and a second overtone ($2\nu_3$) is the transition from ν_0 or ν_3 . Combined bands (e.g., $\nu_1+\nu_2$) are observed when more than one fundamental vibrations are excited simultaneously. Hot bands arise when an already excited vibration is further excited. Hot bands start from an excited energy level (e.g., ν_1 or ν_2) and move to a higher energy level (e.g., ν_1 to ν_2 or ν_2 to ν_3). The main difference between hot bands and overtones is the starting energy level. Fermi Resonance occurs when an overtone or combination band is expected around the same region of a fundamental vibration, resulting in two peaks (Fermi Diad) of nearly the same intensity [178, 179].

The most pronounced peak in a methane hydrate Raman spectrum is the symmetric stretch vibration (ν_1) of guest methane molecules. The band position is strongly affected by the environment surrounding the methane molecules. When methane molecules are enclathrated into a hydrate cage, the peak position shifts: ν_1 vibrations of methane in the gaseous state, in a small hydrate cage, and in a large hydrate cage have band positions at 2914 cm^{-1} , 2905 cm^{-1} , and 2917 cm^{-1} , respectively [168].

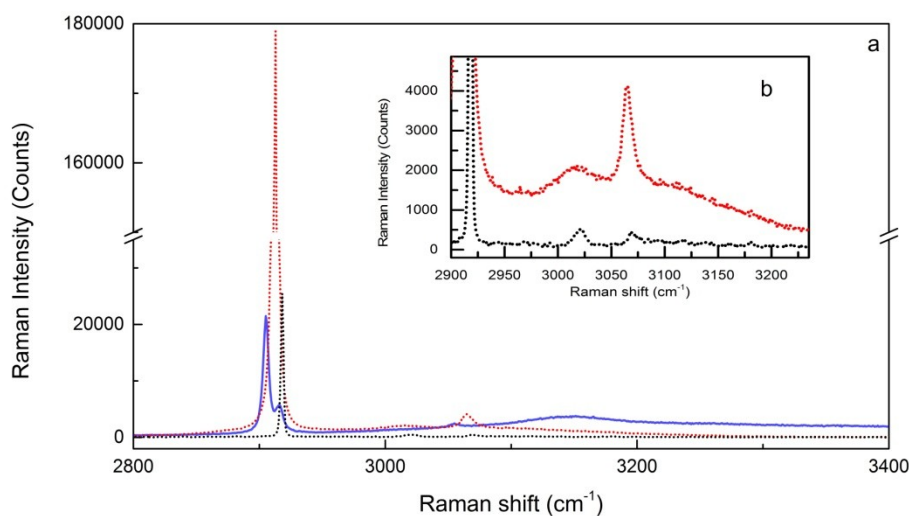


Figure 5.11 a) Comparison of Raman spectra of CH₄ hydrates and CH₄ gas in the high-pressure optical cell b) Expanded view of CH₄ gas showing ν_3 (3028 cm⁻¹) and $2\nu_2$ (3065 cm⁻¹) vibration signal and noise level (ca. 100 counts). — Methane hydrates; - - - Methane gas at 25 MPa and 253K Methane gas at 4.2 MPa and 253K.

At elevated pressures and low-temperature conditions, the spectral peak associated with free methane gas is shifted to lower wavenumbers, causing it under certain conditions to overlap with clathrate methane peaks. Meanwhile, pressure broadening effect of the Raman signal at elevated pressure was also observed (see Figure 5.11a). Methane gas signals were acquired with the same configuration (5% laser power, 5 accumulations and 5s exposure time); a strong Raman response from methane gas at 25 MPa was collected due to more methane molecules being presenting in the confocal plane at elevated pressures. When strongly Raman-active molecules such as methane are present in the laser pathway but not on the confocal plane, a Raman signal from those molecules can still be detected. In the current set-up, where methane gas is always present in the system, the weak hydrate ν_1 signal for one or both of the cages is therefore sometimes obscured. In contrast, the cooperative lattice vibration of the whole water cage at low Raman shift (210 cm⁻¹ see Figure 5.12) provides an additional peak with which to identify gas hydrates under such conditions. This Raman signal does not overlap with the methane vapour signal. It can therefore be used to identify hydrates at temperatures and pressures where the guest intra-molecules vibration mode is hindered by the vapour signal.

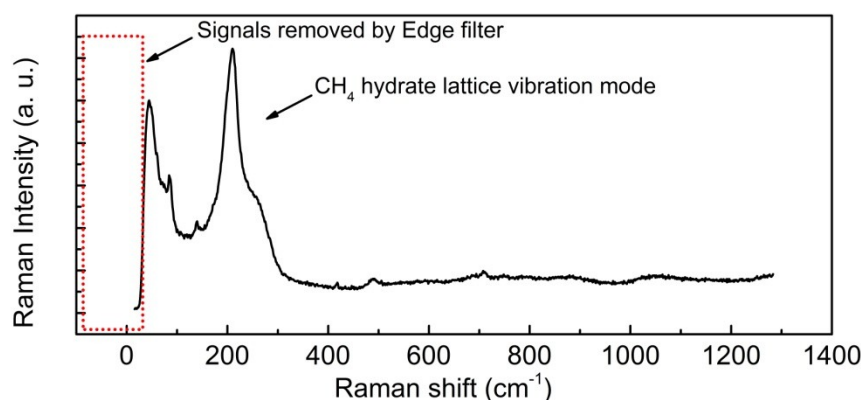


Figure 5.12 Raman spectra of CH₄ hydrates at low Raman shift showing the cooperative lattice vibration peak at 210 cm⁻¹.

Different vibration modes of methane and carbon dioxide molecules in different states have been intensively studied by Raman spectroscopy and theoretical analysis [178-182]. However, the information regarding different vibrational modes of CH₄ and CO₂ is scattered across the literature. In the following sections, high-quality Raman spectra of CH₄ and CO₂ molecules in different states are measured and presented, and the theoretical and observed Raman vibrational modes are also identified.

Figure 5.13C illustrates three Raman peaks of methane gas under pressure. The symmetric stretch vibration (ν_1), the asymmetric stretch vibration (ν_3), and overtone of the asymmetric bending vibration ($2\nu_2$) are all Raman active at 2914 cm⁻¹, 3020 cm⁻¹, and 3067 cm⁻¹, respectively. Other vibrational modes of methane gas are all weakly active and not detected by the current setup, including the symmetric bending vibration (ν_2) at 1526 cm⁻¹, the asymmetric bending vibration (ν_4) at 1306 cm⁻¹, overtone of the bending vibration ($2\nu_4$) at 2600 cm⁻¹, the combination mode ($\nu_4-\nu_3$) at 1720 cm⁻¹, and the combination mode ($\nu_2+\nu_4$) at 2823 cm⁻¹. Figure 5.13A and B show Raman spectra of CH₄ hydrates. The ν_1 vibration of methane molecules is conspicuously affected by the surrounding environment. Therefore, methane gas at different pressures and temperatures, dissolved methane gas (ca. 2910 cm⁻¹, not shown here) and enclathrated methane molecules have different Raman shifts for the ν_1 vibration. Enclathrated CH₄ molecules exhibited different ν_1 vibration frequencies in large cages (2906 cm⁻¹) and small cages (2917 cm⁻¹) in Structure I hydrates (see Figure 5.13B). The intramolecular vibration of the OH bond, as shown in Figure 5.13B, has the symmetric stretch

mode (ν_1) and the asymmetric stretch mode (ν_3), showing overlapped peaks at 3000-3800 cm^{-1} . The lattice vibrational mode at 210 cm^{-1} , shown in Figure 5.13A1, arise from the collective vibration of the clathrate cages in hydrates [180-183].

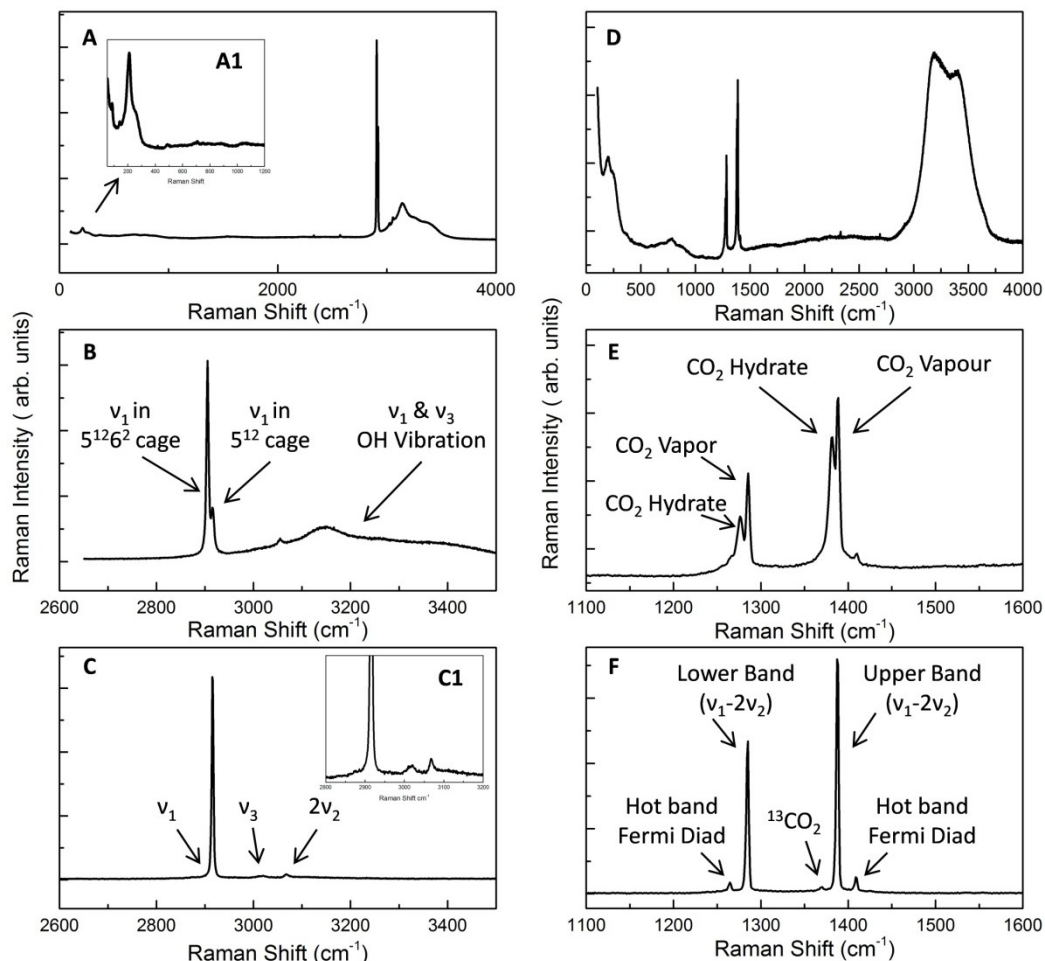


Figure 5.13 Raman spectra of (A) Methane hydrates (A1) Lattice vibration of methane hydrate (B) Expanded view of Methane hydrates (C) Methane Gas (C1) Expanded view of methane gas (D) CO₂ hydrates (E) Expanded view of CO₂ hydrates (F) CO₂ gas.

Carbon dioxide has three basic vibration modes: the symmetric stretch mode (ν_1), the bending vibration (ν_2), and the asymmetric stretch mode (ν_3). The only Raman active fundamental vibrational mode is the ν_1 vibration of carbon dioxide molecules at 1334 cm^{-1} . Other Raman active modes of carbon dioxide molecules include an overtone of the bending vibration ($2\nu_2$) at 1338 cm^{-1} , another overtone of the bending vibration ($3\nu_2$) at 2014.5 cm^{-1} , and a combination band ($\nu_1+\nu_2$) at 1994.9 cm^{-1} . Five Raman peaks of carbon dioxide gas, as shown in Figure 5.13F, are observed including a Fermi Diad of the symmetric stretch mode ($\nu_1-2\nu_2$ Lower Band) at 1285 cm^{-1} , a Fermi Diad of the bending vibration overtone ($\nu_1-2\nu_2$ Upper Band)

Band) at 1265 cm^{-1} , a hot band Fermi Diad of the bending vibration overtone ($3\nu_2$) and a combination ($\nu_1+\nu_2$) at 1265 cm^{-1} and 1409 cm^{-1} [178].

$2\nu_2$ and ν_1 of CO_2 molecules occur at a similar frequency and are perturbed by Fermi resonance, resulting in two bands with nearly the same intensities. Hot bands of $2\nu_2$ and ν_1 also exhibit the Fermi resonance effect. $^{13}\text{CO}_2$ has a concentration of 1.1% in natural carbon dioxide and shows a weak peak at 1370 cm^{-1} . Raman signals of CO_2 hydrates in Figure 5.13D and 4E show a blue shift compared to that of CO_2 vapour signals. Fermi Diads of ν_1 and $2\nu_2$ are both shifted to lower Raman wavenumber in the hydrates. The Fermi Diad peaks of encaged CO_2 molecules do not show separate peaks for the large and small cages, suggesting that CO_2 molecules may not be present in the small cages or that the signal from enclathrated CO_2 molecules in small cages is masked by the vapour phase signal of CO_2 molecules [179].

5.5 Summary

This chapter presents the design, fabrication and testing of a unique pressurised optical cell for Raman spectroscopy and imaging studies of multiphase systems, crystalline solids and soft materials under extreme conditions, such as gas hydrates at high pressures and low temperatures. The cell allows measurements to be conducted over a temperature range 288 to 353 K. Fast temperature response (up to $5\text{ K}\cdot\text{s}^{-1}$), and stable temperature control ($\pm 20\text{ mK}$) are facilitated by using four Peltier elements. To illustrate the performance of the cell, gas hydrate samples were synthesised and analysed *in-situ* by Raman spectra at pressures up to 50 MPa. A large optical path allows macroscopic samples (up to 4.5 mm in size) to be analysed. Such a cell, capable of fitting into the optical systems of a Raman microscope, is not available commercially and can be used to study a wide range of materials which require controlled confinement or are only stable/metastable well away from ambient conditions. Test measurements with methane gas hydrates showed the capability of characterising materials, especially multiphase systems, at different pressure and temperature conditions, the capability of *in-situ* Raman imaging to map out both spatial and temporal variations in composition, structure, and the reaction kinetics of gas hydrate formation will be demonstrated in Chapter 6.

Chapter 6

CH₄-CO₂ Hydrate Gas Exchange Study using Raman Spectroscopy and Imaging

6.1 Overview

Methane hydrates are a potential energy source that occurs naturally in permafrost and along the continental shelves, with the capacity to supply a large component of the world's future energy demands [75]. The recovery of methane (CH₄) hydrates by carbon dioxide (CO₂) injection is a promising route for long-term storage of CO₂ combined with the production of methane from naturally occurring hydrates [15]. Some progress has been made in understanding the fundamental aspects of this process: for example, molecular exchange of hydrate guests has been found to be a diffusion-limited process, influenced by particle sizes, temperature-pressure conditions, and nature of the guest molecules [15, 184]. However, the microscopic exchange mechanism is still a subject of debate [8]. Discrepancies exist in the literature regarding the fraction of recoverable CH₄ and the CH₄-CO₂ exchange rate, even for measurements conducted under similar experimental conditions [184-188]. Raman spectroscopy has been used previously in guest exchange studies to quantify hydration numbers and cage occupancy ratios, but the method was limited to point measurements and the inability to observe the CH₄-CO₂ exchange efficiently at the crystal length-scale [168, 189-194].

In this chapter, a *state-of-the-art* Raman spectroscopy technique with spatial imaging capabilities was utilised to conduct *in-situ* measurements on the CH₄-CO₂ exchange process. Measurements of the replacement process of CH₄-CO₂ exchange were taken at 3 MPa and in the temperature range 269.15 to 277.80 K. Both time-lapsed single point measurements and *In-situ* Raman images were made to reveal the importance of hydrate morphology during the exchange process. Time-resolved Raman results indicated a diffusion-limited guest

substitution process, from which an average diffusion coefficient and cage occupancy ratios were estimated.

6.2 Literature Review

The concept of using CO₂ to replace CH₄ from methane hydrates was first introduced by Ohgaki [195]. Since numerous amounts of methane hydrates are deposited along the continental shelf and in the permafrost, exchanging CO₂ with CH₄ hydrate provides an alternative route to recover CH₄ from naturally occurring methane hydrates while capturing CO₂ in reservoirs; this proposal is supported by the following facts.

1. At pressures below 7 MPa and temperatures below 285 K, which are the conditions of most natural gas hydrate reservoirs, CO₂ hydrates are more stable than methane hydrates. For instance, the equilibrium temperatures for methane hydrates and CO₂ hydrates at 6.89 MPa are 283.15 K and 286.15 K, respectively [195].
2. During the exchanging process, the decomposition of CH₄ hydrates is an endothermic reaction while the formation of CO₂ hydrates is an exothermic reaction. The heat of dissociation for CO₂ hydrates and CH₄ hydrates are 65.22 kJ/mol and 56.84 kJ/mol, respectively [155]. Although studies suggested that an activation energy might be still required to initiate the exchange reaction [196], the exchange process is self-sufficient in terms of the reaction heat. If the exchange occurs fast enough, in an isobaric environment, the excess heat increases the surrounding temperature, leading to accelerated dissociations of methane hydrates.

Macroscopic experiments of CH₄-CO₂ exchange were conducted by measuring the composition of vapour or liquid phase during the exchange process [185, 196, 197]. The initial composition of CH₄ hydrates was calculated by pressure-temperature changes based on equations of state, and the CH₄ gas phase was replaced by liquid or gaseous CO₂ at the beginning of the exchange process. During the gas exchange, the composition of the CO₂ rich phase was constantly monitored using gas chromatography. Results suggested that the exchange rate and recovery ratio of methane from the hydrates strongly depended on the

temperature and pressure conditions. When the temperature-pressure conditions were close to or outside of the stable phase boundary of CH₄ hydrates, higher exchange rates were obtained. The exchange rate was also observed to decrease with time, which was attributed to a reducing mass transfer rate as a CO₂ hydrate layer formed. Macroscopic exchange experiments in porous media [198, 199] also suggested that porous media enhanced the exchange rate, possibly due to the increased available surface area in the porous media. In a well-controlled macroscopic study conducted by Lee and co-workers [184], the exchange was performed with nearly fully converted hydrate particles (conversion > 95 %) and analysed by an online gas chromatography. A two-step exchange process, a fast surface reaction and a diffusion-limited step, was observed and correlated by Avrami and shrinking core models. Results also suggested that temperature was an important factor; the size of the initial hydrate particle, which affected the surface area, was also important for the exchange process.

Whereas macroscopic measurements give indirect information about the composition of gas hydrates, microscopic techniques (e.g., nuclear magnetic resonance spectroscopy, magnetic resonance imaging, and Raman spectroscopy) measure the properties of the hydrate/solid phase directly and provide structural information like hydrate types and cage occupancy ratios.

For example with nuclear magnetic resonance (NMR) measurements, ¹H and ¹³C exhibit different chemical shifts for encaged methane molecules in large and small cages in sI type hydrates and the peak areas with their relative chemical shifts can be related to the amount of methane molecules, enabling the identification of hydrate type (e.g., structure I and II) and quantitative analysis of cage occupancy ratios during the exchange. Lee et al. [200] studied the kinetics of replacing methane hydrates with CO₂ using solid-state NMR. It was found that the relative cage occupancy ratio of large to small cages dropped during the exchange process. Although NMR spectroscopy could not distinguish between CO₂ molecules in the large and small cages of sI hydrates, a quantitative analysis of mixed hydrates prepared with different feed gas compositions suggested that CO₂ molecules preferentially occupied the large cages of sI hydrates. These workers also proposed that a theoretical limit of 64% for carbon dioxide

replacement within methane hydrates. Park et al. [201] also studied CH₄ hydrate exchange with binary gas mixtures by NMR techniques. A binary mixture of N₂ (80 mol%) and CO₂ (20 mol%) was used to exchange with methane hydrate, yielding a recovery ratio of 85% of methane hydrates at 3.5 MPa and 274.15 K. The NMR measurements indicated that 23% of encaged methane molecules were replaced by N₂ and 62 % by CO₂.

In NMR measurements, averaged properties of samples contained in a cylindrical tube (typically a few millimeters in length) are analysed. In contrast, the magnetic resonance imaging (MRI) technique can give a 3D visualisation of the exchange process at sub-millimetre scale and a quantitative analysis of the CH₄-CO₂ exchange process. The MRI technique monitors the changes in the relaxation time of protons between hydrate and the fluid phase and distinguishes between the hydrates and its precursors (gas and water), allowing quantification of methane hydrate formation and CO₂ hydrate exchange. Ersland and co-workers [202] conducted hydrate exchange experiments at 277 K and 8.27 MPa, monitored by MRI. Results suggested that CH₄-CO₂ exchange occurred spontaneously and heterogeneously in a sandstone sample, resulting in a conversion of 50 % of methane hydrates in 300 hours.

Raman spectroscopy measures the vibrational modes of different molecules. Since the vibrational energy levels are unique to each molecule, Raman spectra provide a fingerprint of a particular molecule and elucidation of molecule structures. Raman spectroscopy also distinguishes molecules in different states (e.g., liquid, vapour, encaged) [189]. It has been used to identify structural information on gas hydrates [168] and hydration numbers for guest molecules [190]. More recently, Raman spectroscopy was applied to detect dissolved methane gas in deep sea areas [191] and to examine methane hydrate core samples from hydrate reservoirs [192-194]

Yoon et al. [186] used Raman spectroscopy to study the CH₄-CO₂ exchange process at a pressure of 3 MPa and a temperature of 278 K. Methane hydrate particles, originating from ice particles, with a size range of 100 µm to 250 µm were exposed to CO₂. An overall conversion of 60 % was achieved in 150 hours. The authors also measured fast reaction and

high conversion rates due to the exchange being executed at temperature and pressure conditions, where methane hydrates are unstable. Komai et al. [187] also conducted similar experiments at 276 K and 3.5 MPa under an atmosphere of CO₂. A high conversion rate (98% within 12 hours) was obtained due to the unstable temperature-pressure conditions for methane hydrates. Ota and co-workers [188, 203] studied CH₄-CO₂ exchange with an *in-situ* Raman spectroscopy technique when liquefied CO₂ reacted with methane hydrates. Results showed that the Raman intensity of large and small cage signals both decreased with the large cage signal depleting faster than that of the small cages. It was also found that CO₂ could replace about 65 % methane from CH₄ hydrates.

For the aforementioned CH₄-CO₂ exchange experiments, a direct comparison of the recovery ratios is not possible due to the differences in conditions of pressure, temperature and available surface area. However, obvious discrepancies in exchange rate exist among the above studies; for example, Lee et al. [184] attained a 22% to 33% conversion at ca. 9 MPa and 275 K in 125 hours ; Horiama et al. [185] obtained 13% conversion at 3.85 MPa and 275 K in 800 hours; Yoon et al. [186] achieved 60% conversion at 3 MPa and 276 K in 150 hours; Komai [187] found 98% conversion at 3.5 MPa and 276 K in 12 hours; Ota et al. [188] achieved 21% conversion at 3.34 MPa and 275.2 K in 150 hours.

Microscopic measurements (i.e., MRI, NMR, and Raman spectroscopy) provide a powerful means to elucidate the molecular structure of gas hydrates. However, the resolution has been limited to millimetre scale (NMR spectroscopy) and sub-millimetre scale (MRI). Raman spectroscopy has the potential to provide high-resolution measurements down to micron scale, but the existing measurements have been limited to single point measurements, which may be unable to illustrate the impact of the heterogeneity of hydrate particles and the spatial distribution of different gas hydrates.

6.3 Materials

Research grade methane and CP grade carbon dioxide were supplied by BOC with a specific minimum mole fraction of 0.99995. Deionised water with an electrical resistivity higher than

18 M Ω ·cm at 298 K was obtained from a piece of reverse-osmosis apparatus (Millipore, Direct-Q3). Heptadecafluoro-1-decanethiol and ethanol (Sigma-Aldrich) were of purities 96% and 95%, respectively.

6.4 Apparatus

The high-pressure cell described in Chapter 5 was used in this work. The Raman spectroscopy (imaging) studies reported here were carried out in the Laboratory of Professor Eric May in the school of Mechanical and Chemical Engineering, University of Western Australia (Perth). Raman spectra were obtained using a Renishaw InVia Reflex Raman Spectrometer equipped with a 532 nm diode laser (Nd:YAG Laser) for excitation with a maximum output power of 100 mW at the source (Shown schematically in Figure 6.1). Neutral density filters regulated the output power reaching the samples to prevent overheating and decomposing the hydrate samples. All measurements were performed with an Olympus Plan semi-apochromatic 20 $\times$ objective (numerical aperture of 0.4), providing a theoretical spot size of 1.4 μ m under confocal mode. 180° backscattered Raman signals were collected and collimated from the same spot area. An edge filter eliminated elastically scattered signals and enabled the Stokes Raman signal to be observed over the spectral range from 50 cm⁻¹ to 5400 cm⁻¹. The inelastically scattered Raman signal was focused through a slit (65 μ m width) and dispersed by a holographic diffraction grating with 2400 grooves/mm onto a thermoelectrically cooled charge-coupled device (CCD) detector working at a temperature of 172 K.

An automated XYZ translation stage with a resolution of 0.1 μ m facilitated a raster scan of an area of interest over the hydrate samples. Raman shifts were calibrated periodically on an internal reference silicon wafer. All control and data acquisition of the Raman system were realised by Wire 3.4 software. The temperature was collected using the Agilent VEE program through an Agilent 34970A data logger and the pressure was monitored using a transducer via an RS485 interface. The Raman enclosure was continuously purged with compressed nitrogen, and a Peltier-based condenser was placed inside the enclosure to collect moisture at 256 K.

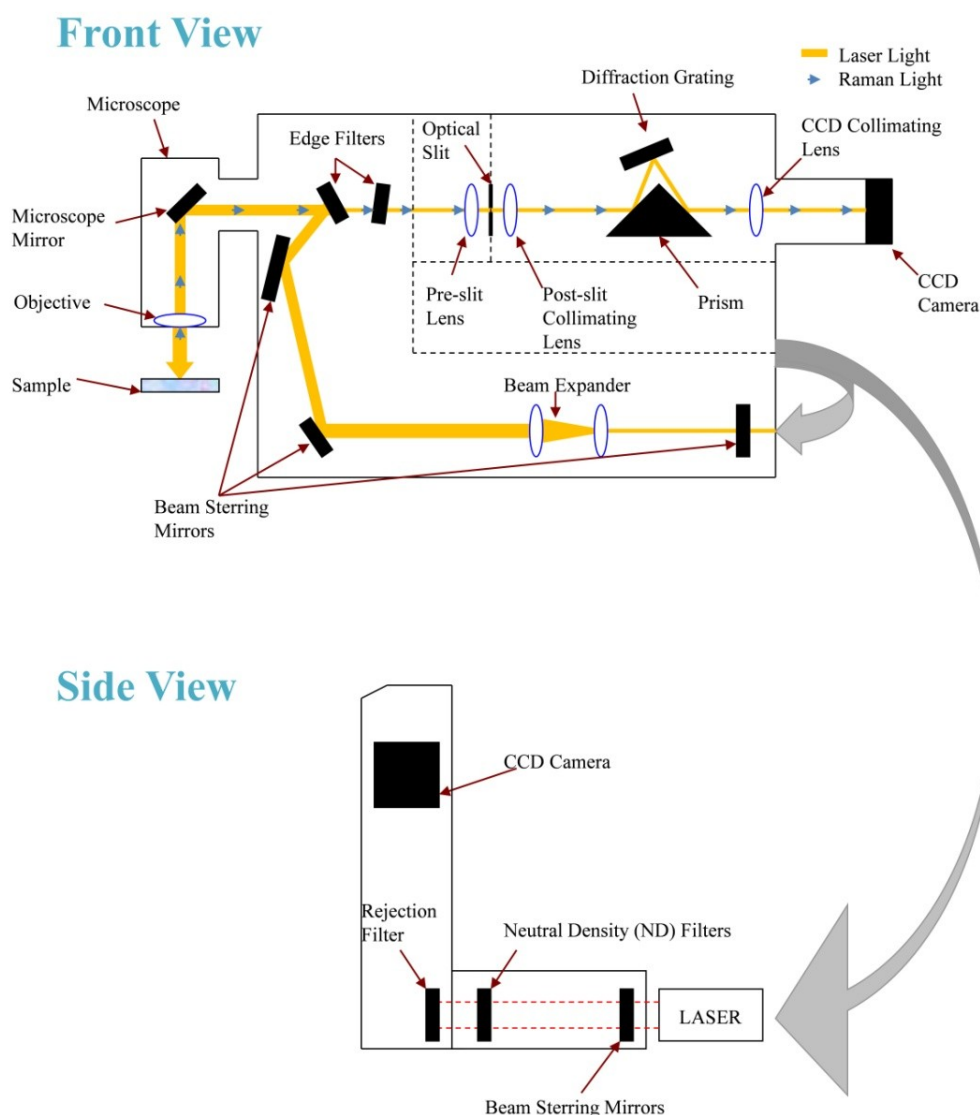


Figure 6.1 Schematic of Renishaw InVia Reflex Raman spectrometer. “© Copyright Renishaw plc. All rights reserved. Image reproduced with the permission of Renishaw.”

All Raman measurements unless specified were conducted on an XY plane scanned over the half height (Z axis) of the hydrate samples. Raman images of CH_4 hydrates and CO_2 hydrates were scanned every 6 to 8 hours. Raman spectra, in SynchroScan mode with an extended spectral range, were acquired at single points within the sample between the acquisition of Raman images. To monitor the time-dependent exchange process, Raman spectra of CH_4 hydrates and CO_2 hydrates at a range of fixed spots along a one-dimensional diffusion path from the surface to the centre of the hydrate crystal were obtained every 30 minutes. Continuous scans with the high laser power were found to be destructive to hydrate samples, so the incident laser with 10 mW power was dispersed to a line using a cylindrical lens and an

exposure time of just 3.24 s was used for the Raman imaging mode. A laser power of 1 mW and an exposure time of 10s were applied in obtaining the single spot SynchroScan spectra over a spectral range of 50 cm⁻¹ to 4000 cm⁻¹. Raman peaks of CH₄ hydrates centred at 2906 cm⁻¹ and CO₂ hydrates centred at 1381 cm⁻¹ were used to construct the 3D Raman images.

6.5 Hydrate Preparation and Operating Procedures

To study the effect of hydrate morphology on the CH₄-CO₂ exchange process, three different types of hydrate crystals were synthesised in the high-pressure cell, namely (transparent) single crystal CH₄ hydrates, semi-transparent defective crystal CH₄ hydrates and polycrystalline CH₄ hydrates.

Polycrystalline CH₄ hydrates were formed isobarically by placing a water droplet (size around 400 µm in diameter) on a hydrophobic surface pressurising the cell with methane at 15 MPa and then oscillating the temperature between 278.15 K and 248.15 K [71]. Morphologies of polycrystalline hydrates were usually unpredictable, but they normally maintained the original hemispherical shape of the water droplets. As a consequence of the amorphous nature of polycrystalline hydrates, no transparency was observed under a white-light microscope. In contrast, transparent single crystal hydrates were formed isothermally at 14 MPa by using a much smaller thermal driving force (ca. 3 K). The process is illustrated in Figure 6.2a (Route A). The resulting crystals showed hexagonal and tetragonal shapes and were completely transparent under a white-light microscope. The semi-transparent crystals were formed under slightly higher thermal driving force (ca. 5 K to 10 K). They had irregular crystal shapes and were significantly less more opaque than the transparent hydrate single crystals. This is probably due to the presence of defects which scatter light.

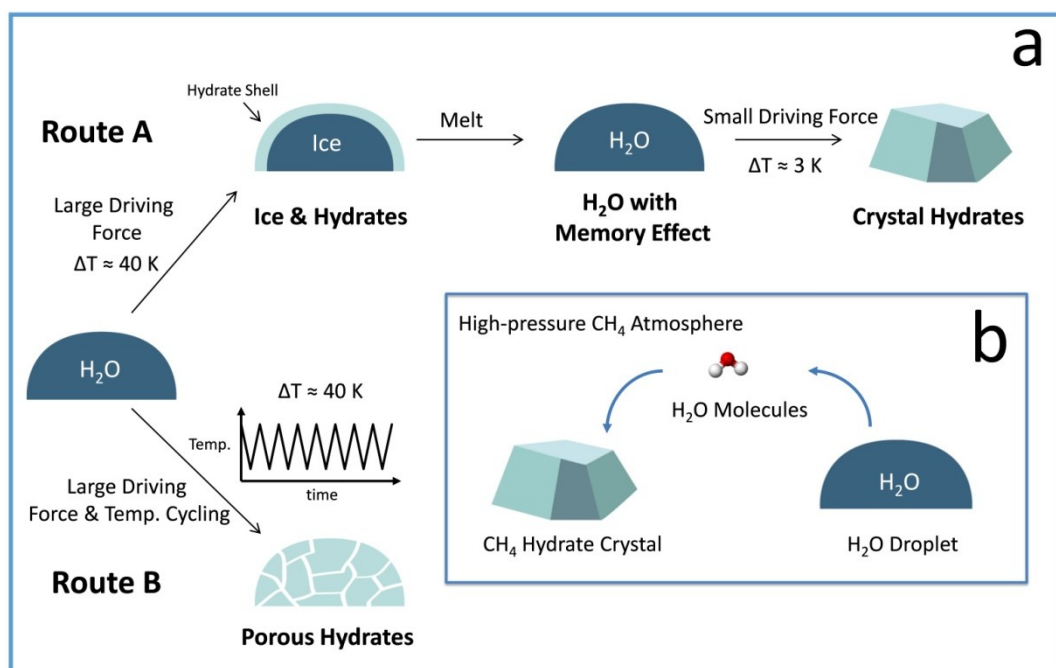


Figure 6.2 Mechanism of hydrate crystal growth. Route A: (a) Formation of porous hydrate under large driving force followed by melting and formation of crystal hydrates under small driving forces with the assistance of the hydrate ‘Memory Effect’. (b) Further growth of methane hydrate crystals was achieved by consuming water molecules from the vapour phase, and non-reacted water droplets acted as water reservoirs. Route B: Formation of porous polycrystalline hydrates under large thermal driving force with temperature cycling.

6.5.1 Formation of Porous Polycrystalline Hydrates

Porous hydrates were formed with large thermal driving forces through an oscillating temperature process (see Figure 6.2a Route B). A few deionised water droplets (ca. $0.1\ \mu\text{L}$ each) were loaded into the cell which was subsequently pressurised with methane to a constant value of 15 MPa. The temperature was set to oscillate between 278.15 K and 248.15 K with a ramping rate of $3\ \text{K}\cdot\text{min}^{-1}$. A large excess driving force (ca. 40 K) was provided to ensure the spontaneous nucleation of gas hydrates. The amount of ice was reduced in each oscillating cycle, and water was expected to be fully converted into hydrates within 20 hours. With a large driving force, hydrates tended to migrate and spread out on hydrophilic surfaces. Hydrophobic surfaces (oxidised silver surface or fluorocarbon coated silver surface) helped to maintain the shape of the hydrate particles. The hydrophobic surface was prepared by exposing a polished sterling silver surface to air at room temperature for three weeks. When the sterling silver, which contains around 7.5% copper, was exposed to excess heat,

extensively oxidised copper generated a notable Raman background contribution. The hydrophobicity could be further improved by exposing the polished sterling silver surface to 0.1M heptadecafluoro-1-decanethiol in ethanol solution to form a monolayer of fluorocarbon which did not show a background contribution to the Raman spectra.

6.5.2 Formation of Transparent Single Crystals and Semi-Transparent Crystals

Forming a single crystal methane hydrate requires a carefully controlled formation process. Such controls can be achieved by providing a small thermal driving force, selecting proper temperature-pressure conditions in relation to the equilibrium conditions of CH_4 hydrates, or by limiting the supply of water molecules.

Transparent crystals were formed isobarically at 14 MPa. A few droplets of deionised water (ca. 0.02 μL each) were loaded into the cell at 288.15 K. The cell was subsequently sealed, purged, and pressurised. The cell temperature was ramped down to 248.15 K, then heated to 289.65K at a rate of 2 $\text{K}\cdot\text{min}^{-1}$, and then held at 285.65K. The first cooling and heating cycle aimed at forming and melting hydrates to generate a hydrate “Memory Effect” for the water sample [104]. A relatively small driving force (around 3 K at 14 MPa) was then provided under static conditions. Crystal hydrates and amorphous hydrates appeared randomly with various induction times (see Figure 6.2a Route A). Transparent hydrate crystals originated from hexagonal plate crystals and grew into tetragonal prism crystals and hexagonal prism crystals. Figure 6.3 illustrates the resulting hexagonal and tetragonal hydrate crystals.

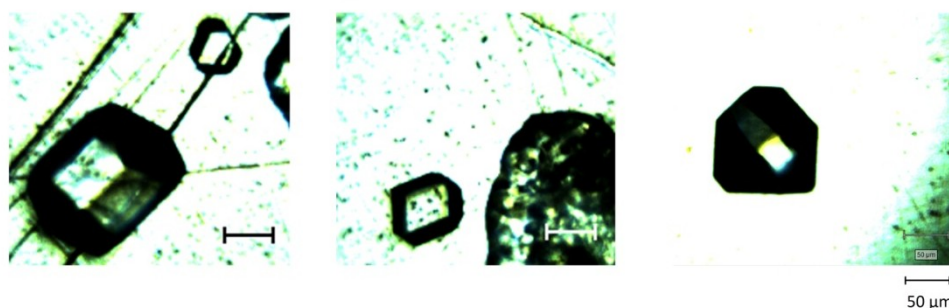


Figure 6.3 Methane hydrate single crystal shapes

Semi-transparent crystals also originated from hexagonal crystal plates. Defects on the crystal surfaces were introduced by using a relatively large driving force (ca. 5 K to 10 K at 14 MPa) during the crystal growth process. Under such large driving forces, crystals grew preferentially on some facets, resulting in irregular shaped hydrates (see Figure 6.4).

In contrast with the formation of polycrystalline hydrates, the single crystal growth was favoured by (i) a small thermal driving force, (ii) restricted amount of water available and controlled slow uptake of water via the vapour phase transport, and (iii) hydrophilic surfaces. Methane hydrate crystals might evolve from the original locations of water droplets or submicron grooves which acted as heterogeneous nucleation sites on the hydrophilic surface and were expected to appear within 24 hours. However, the actual induction time of the heterogeneous nucleation was unpredictable. Even under small driving forces (ca. 3 K), when the original water droplet size was larger than 300 μm , polycrystalline hydrates might be formed due to the excessive amount of water available locally at the crystal growth site, rather than single crystals which form from much smaller droplets (ca. 50 μm or less). It was also found that oscillating the cell temperature below the equilibrium temperature helped to anneal imperfect hydrate crystals, slowly increasing their transparency.

When small hydrate crystals appeared in the cell, further growth of the crystals was achieved by consuming water vapour from the high-pressure vapour phase. Water has a fairly small vapour pressure under the experimental conditions and on account of the pressure, the temperature, and the cell volume, the total amount of water available from the vapour phase was orders of magnitude smaller than the amount of water required to form a crystal with a diameter of several hundred microns. So water droplets that were not converted into hydrate acted as water reservoirs for vapour phase transport of water molecules into the growing hydrate crystals at a low and controlled rate. It was observed that unconverted water droplets in the high-pressure cell shrank steadily, and methane hydrate crystals continued to grow until all free water in the cell was consumed (see Figure 6.2b). Further evidence of the above scenario is given in Figure 6.4. No free water was available locally within the growing crystal, and the hydrate crystal was growing slowly over time via vapour phase transport of both

water and methane molecules. When unreacted water droplets were mostly consumed at 26 hours, crystal growth slowed down dramatically.

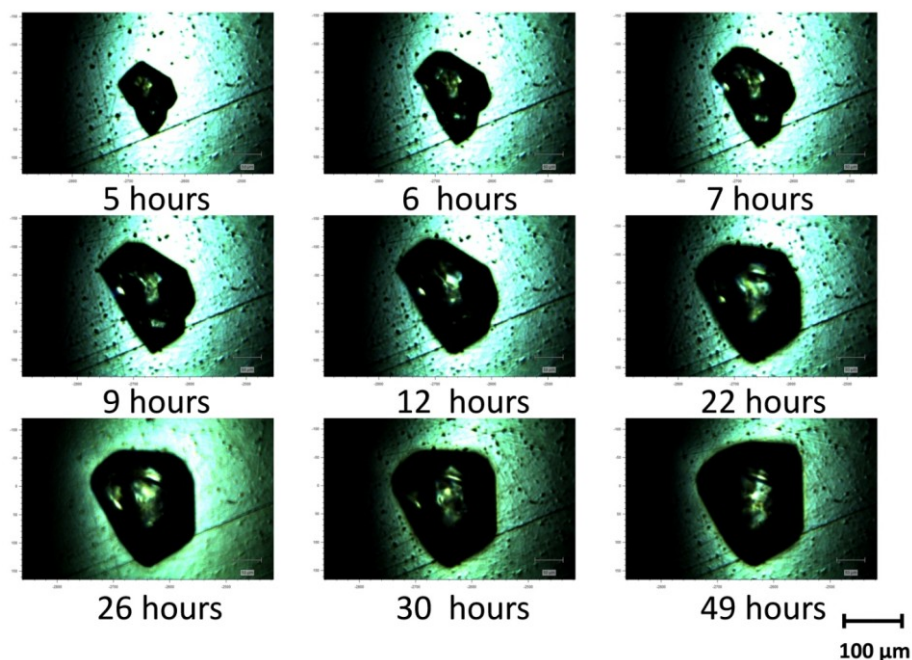


Figure 6.4 Time-lapsed crystal growth images showing irregularly shaped methane hydrate crystal grown under a large thermal driving force (ca. 15K). Time indicates the duration since the start of the isothermal dwell stage at 14 MPa.

6.5.3 $\text{CH}_4\text{-CO}_2$ Exchange Conditions

Once the methane hydrates had been synthesised, the conditions in the cell were changed in order to monitor the exchange of methane by carbon dioxide. The pressure and the temperature in the cell were reduced to 3 MPa and 269.15 K, respectively. A high-pressure pump (Teledyne Isco, model 260DM) with a capacity of 260 cm^3 filled with CO_2 was connected to the cell and set to constant pressure mode at 3 MPa. Two high-pressure valves, between which the dead volume was estimated to be about 50 μL , were connected in series downstream of the cell. The Isco pump continuously delivered CO_2 gas into the cell while the two downstream valves were opened and closed successively. During the gas exchange process, Raman spectra of methane gas and carbon dioxide gas were continuously collected. The residual concentration of methane in the cell after displacement by CO_2 was estimated to be less than 1 mol%. During the exchange experiments, the cell was kept isothermal at each set point for 24 hours before being ramped to another temperature at a rate of $2 \text{ K} \cdot \text{min}^{-1}$. Two

initial three-day exchange experiments were conducted isobarically at 3 MPa with a poly-crystal (Experiment 1) and a semi-transparent crystal (Experiment 2) at (269.15 K, 271.15 K, and 273.35 K) and (273.50 K, 276.30 K, and 277.80 K), respectively. Temperatures were held constant for 24 hours at each set point. Other exchange experiments (Experiment 3 to Experiment 6) typically lasted for five days at 3 MPa. The temperature was set to 269.15 K, 271.15 K, 273.50 K, 276.30 K, and 277.80 K, respectively. At the end of each isotherm, evolved methane gas was purged again with CO₂. However, in the light of small quantities of methane hydrate present in the reactor, the evolved methane gas had negligible effect on the exchange process.

6.6 Results and Discussion

6.6.1 Laser Heating Effect of Hydrate Samples

Raman spectroscopy is often regarded as a nondestructive technique. Due to the inherent weak intensity of Raman signals, a sensitive detector and sometimes a strong laser are used to detect the weakly scattered Raman signal. In a Raman measurement, laser source is confined to a small spot (typically a few microns), which can result in a localized temperature increase or even sample decomposition during the measurement. The heating effect from lasers is affected by a few factors including laser power, spot size (objective numerical aperture), diffraction coefficient, absorption coefficient, temperatures and thermal conductivity of the sample. Extra caution should be taken when sensitive samples like hydrates are studied.

The lattice vibration mode of hydrates at 210 cm⁻¹ was used to measure the stability of hydrate samples under continuous Raman scans with a 532 nm green laser and a 20X objective (N.A. 0.25) providing a laser spot size of 2.6 μm. Raman signals obtained using 10 mW of laser power showed a steady response over the experiments (see Figure 6.5a). High power lasers (50 mW in Figure 6.5b and 100 mW in Figure 6.5c) were found to be destructive to the hydrate samples. Samples were heated by continuous scans under 50 mW and 100 mW laser power, leading to an increased Raman response. Overheated samples showed a decreased Raman response which is a sign of losing the clathrate structure and decomposition of hydrates. Similar conclusions were made with ν₁ vibration of CH₄ molecules in large cages

at 2905 cm^{-1} . It was also found that a single 5 s exposure of 100 mW laser power with a high numerical apertures objective (N.A. 0.4) was destructive to hydrate samples. Defocusing laser function is also helpful to spread laser power to a wider range in case the incremental steps of laser power provided by neutral density filters are not appropriate for certain measurements.

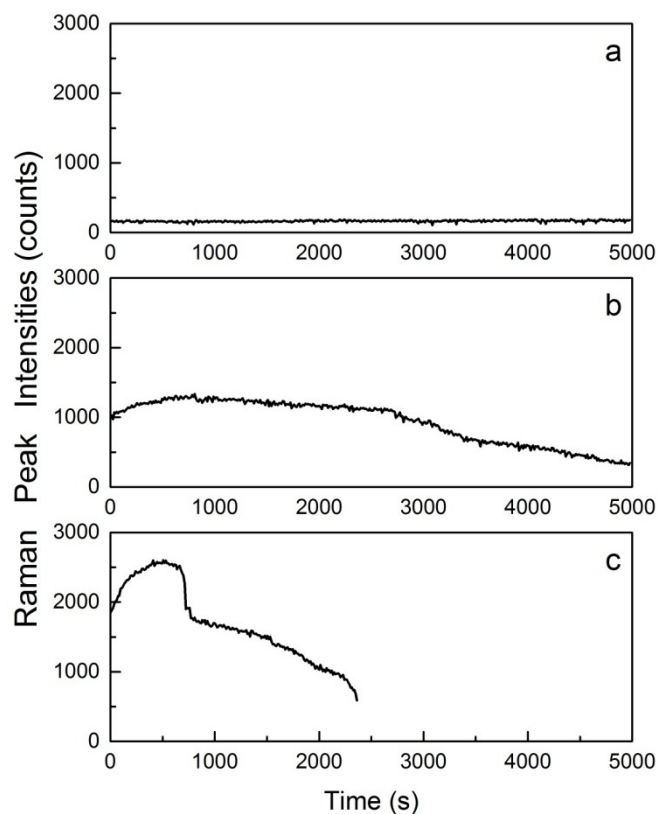


Figure 6.5 Variation of peak Raman Intensity for the lattice vibration mode under a continuous laser scan for a hydrate sample with different laser powers: a) 10 mW laser power, b) 50 mW laser power, c) 100 mW laser power (Exposure time was set to 1 s and 10 accumulations were collected for all spectra)

6.6.2 Raman Point Measurements of $\text{CH}_4\text{-CO}_2$ Hydrates Exchange

Laser powers were set to a minimal level to prevent heating effects for both Raman point (1 mW laser, 10 s exposure time, spot focus) and Raman imaging (10 mW laser, 3.24 s exposure time, line focus) measurements. Under the above settings, Raman responses from point measurements were 10 to 15 times stronger than those from Raman images using the line source.

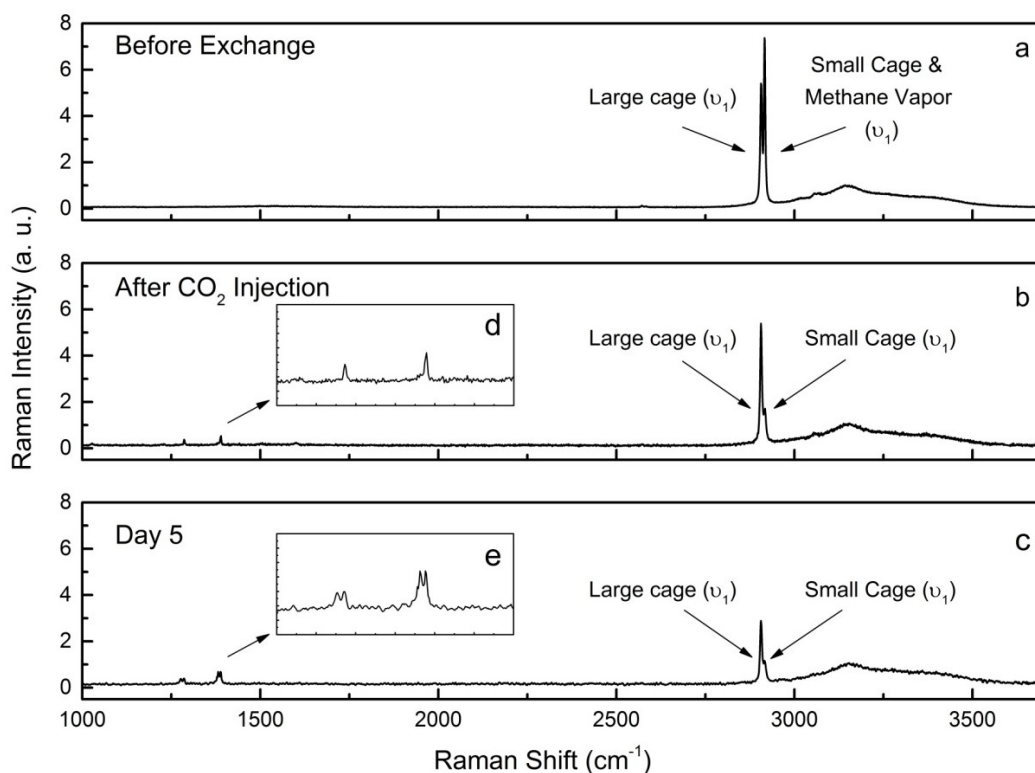


Figure 6.6 Raman spectra during a $\text{CH}_4\text{-CO}_2$ exchange experiment a) before the exchange b) after CO_2 injection c) after a five-day exchange process d) expanded view showing CO_2 vapour spectra e) expanded view showing CO_2 vapour signal and CO_2 hydrate signal.

Figure 6.6 illustrates typical Raman spectra obtained during a five-day exchange experiment on a CH_4 crystal with defects (semi-transparent hydrate). Raman spectra were acquired at the half height of the hydrate crystal and $15\ \mu\text{m}$ from the edge of the crystal. The out-of-focus ν_1 vibration peak of CH_4 molecules in the vapour phase was also present in the Raman spectrum (see Figure 6.6a). Since the ν_1 vibration mode of CH_4 molecules was strongly Raman active and existed along the laser pathway, the scattered Raman signal might migrate to the focal plane and contribute to the overall spectrum. After the gas exchange process, CO_2 molecules in both the vapour phase and the hydrate phase showed weak Raman responses compared to CH_4 molecules (see Figure 6.6d and 5e). During the exchange process, Raman intensities of CH_4 molecules in both large and small cages decreased. The peak areas of the Raman spectra were calculated by fitting Gaussian-Lorentzian curves to representative Raman peaks. The cage occupancy ratio was calculated by the relative peak area ratio of the CH_4 large and small cage signals.

At the end of the three-day exchange experiment (Experiment 2), the cage occupancy ratio of CH₄ hydrates decreased significantly around the edge of the hydrate crystals where most of the gas exchange occurred (see Figure 6.7). Unreacted CH₄ hydrate, which was located at the middle of the hydrate crystal, showed a cage occupancy ratio of 3.04 ± 0.03 . The cage occupancy ratio decreased steadily to 0.92 (1.15 for Experiment 3) when the focal point moved to the edge of the crystal. The relative cage occupancy ratio of the resulting CO₂ hydrates cannot be resolved by the Raman spectra. However, during the exchange process, the intensity of enclathrated CO₂ increased, and the large/small cage occupancy ratio of CH₄ hydrates dropped, suggesting that CO₂ molecules preferentially occupied the large cages of the methane hydrates. On the timescale of the exchange experiments conducted, the large clathrate cages of CH₄ hydrates were not fully replenished by CO₂ molecules, even at the outer surface of the hydrate particle, leading to coexisting CH₄-CO₂ hydrates on the surface of the hydrate particles.

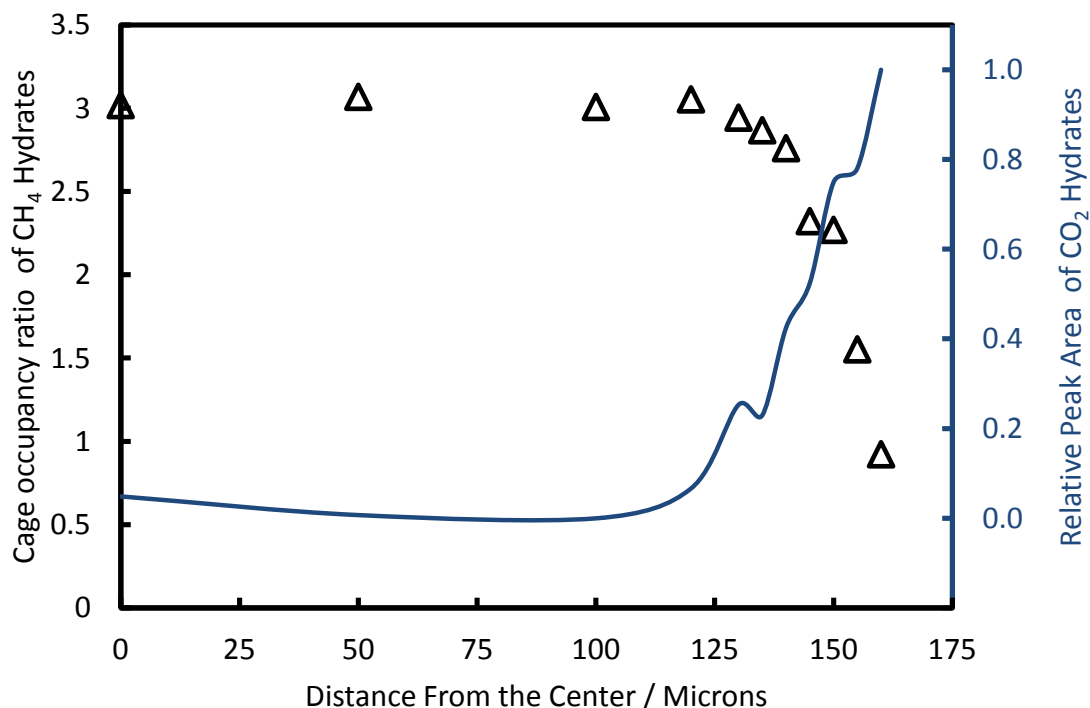


Figure 6.7 Cage occupancy ratio of CH₄ hydrates in large cages (2906 cm⁻¹) and small cages (2915 cm⁻¹) as a function of position across the crystal from point measurements after a three-day exchange experiment on a hydrate crystal with defects (Left axis). Raman intensity of CO₂ hydrates (peak area) at 1381 cm⁻¹ over OH bond (peak area) at 3020 cm⁻¹ (Right axis); Δ , CH₄ cage occupancy ratio of large cages and small cages; —, relative CO₂ peak area.

Due to the heterogeneity of the semi-transparent hydrate particles, the absolute signal intensity of CH₄ hydrates and CO₂ hydrates was strongly altered by the defects and uneven surfaces on the crystal. The relative ratio between the peak areas of hydrates and the peak areas of the OH vibration at 3020 cm⁻¹ was used to mitigate morphology and temperature induced variations in the Raman responses. During a five-day exchange experiment (Experiment 3) on a semi-transparent crystal, the relative CO₂ hydrate signal increased gradually (see Figure 6.8 and Figure 6.10), and the relative CH₄ hydrate intensity showed a steady decrease (see Figure 6.9 and Figure 6.11). The four-dimensional images (see Figure 6.8 and Figure 6.9) illustrated the combined spatial and temporal variations of CO₂ and CH₄ hydrates during the gas exchange process. Although the Raman peaks of CO₂ and CH₄ hydrates were present at different frequencies of a Raman spectrum (see Figure 6.6), the time-lapsed Raman measurements show that the increase of CO₂ hydrate Raman intensity was consistent with the net consumption of CH₄ hydrate Raman intensity both spatially and temporally.

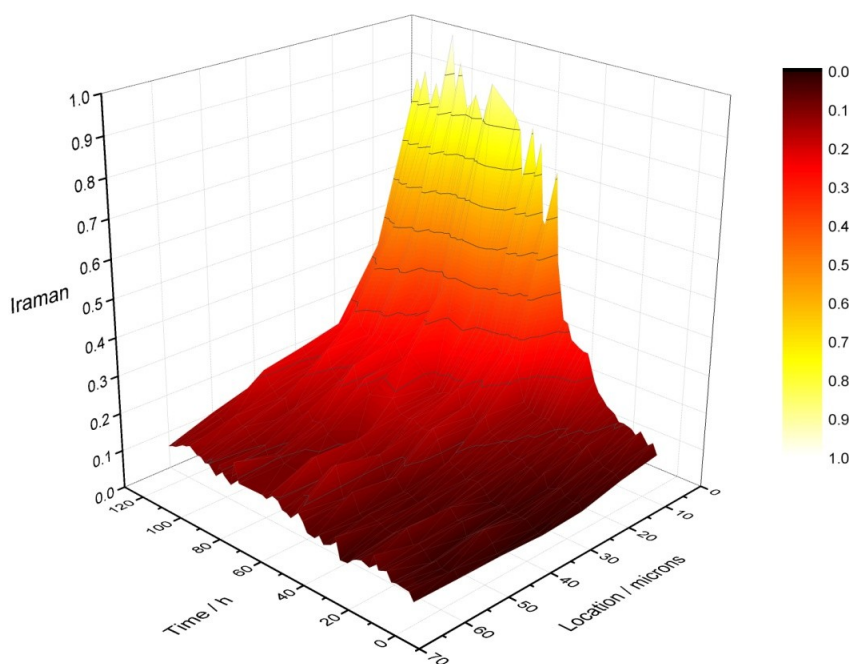


Figure 6.8 Time-lapsed Raman intensity of CO₂ hydrates (peak area) at 1381 cm⁻¹ over OH bond (peak area) at 3020 cm⁻¹ during an exchange experiment (Exchange 3) on crystal CH₄ hydrates with defects. The intensity was normalised to the largest Raman intensity of CO₂ hydrates during the experiment. Location in microns indicate the distance from the edge of the hydrate particle. Measurements were conducted at the half height (Z axis) of the hydrate particle along a line at 3 MPa.

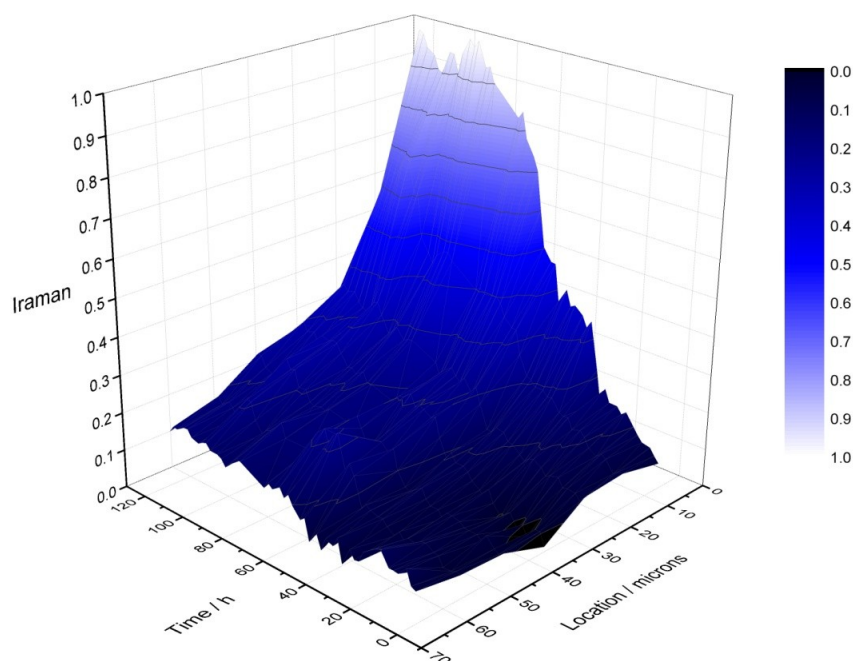


Figure 6.9 Time-lapsed net decrease of CH_4 hydrate Raman intensity (peak area) at 2906 cm^{-1} over OH bond (peak area) at 3020 cm^{-1} during an exchange experiment (Exchange 3) on crystal CH_4 hydrates with defects. The intensity of CH_4 hydrates was subtracted by and normalised to the largest Raman intensity of CH_4 hydrates during the experiment. Location in microns indicate the distance from the edge of the hydrate particle. Measurements were conducted at the half height (Z axis) of the hydrate particle along a line at 3 MPa.

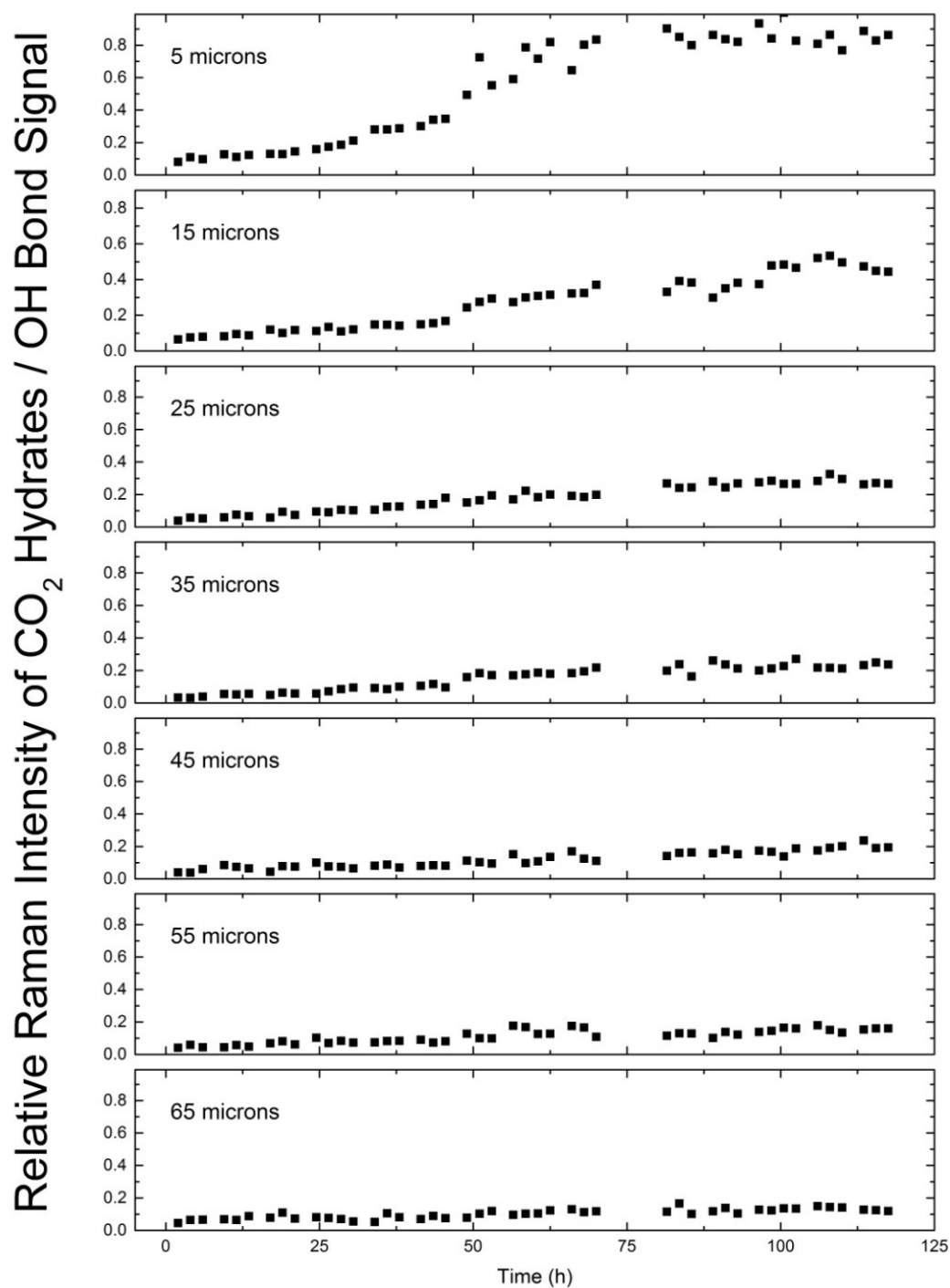


Figure 6.10 Raman intensity of CO_2 hydrates (peak area) at 1381 cm^{-1} over OH bond (peak area) at 3020 cm^{-1} during an exchange experiment on crystal CH_4 hydrates with defects. Numbers in microns indicate the distance from the edge of the hydrate particle. Measurements were conducted at the half height (Z axis) of the hydrate particle along a line at 3 MPa.

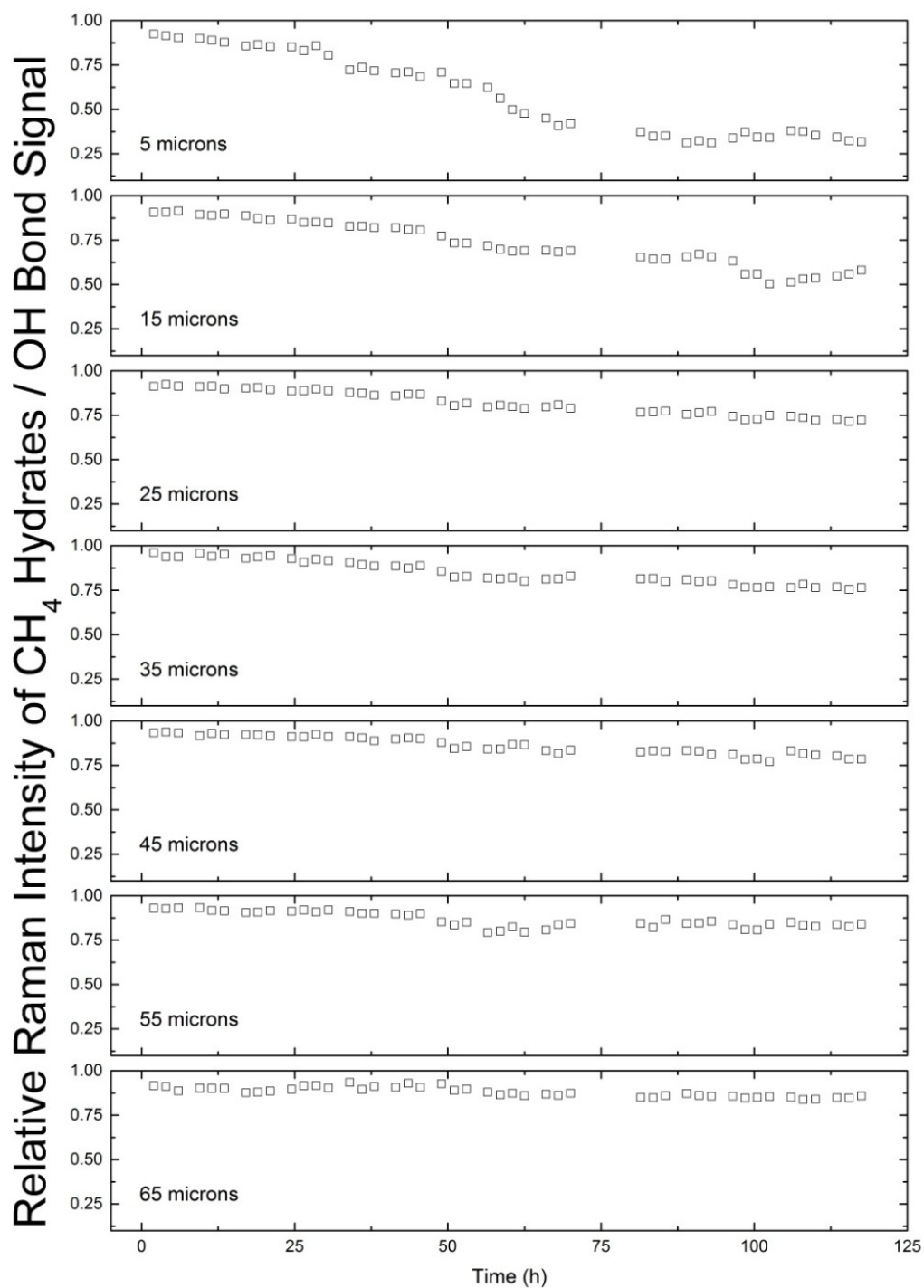


Figure 6.11 Raman intensity of CH_4 hydrates (peak area) at 2906 cm^{-1} over OH bond (peak area) at 3020 cm^{-1} during an exchange experiment on crystal CH_4 hydrates with defects at 3 MPa. Numbers in microns indicate the distance from the edge of the hydrate particle. Measurements were conducted at the half height (Z axis) of the hydrate particle along a line.

The rate of exchange, as shown in Figure 6.10 and Figure 6.11, was relatively slow during the initial two days at 269.15 K and 271.15 K (equilibrium conditions are shown in Figure 2.4 and Figure 6.18), when the kinetic driving force of the exchange process was comparatively small. When the temperature was ramped to 273.50 K on the third day, CO₂ hydrate started to accumulate more rapidly on the surface of the hydrate particle, and the intensity of methane hydrates began to decrease. Based on the point measurements of CO₂ hydrates and CH₄ hydrates, the exchange mainly occurred within 50 μm from the edge of the particle. A slight amount of CO₂ hydrate signal from inner parts of the hydrate particle came from CO₂ hydrates presented in the laser pathway. It can be seen that the exchange temperature, reflecting the thermal driving force for the exchange process, had a distinct effect on the exchange rate.

Two factors contributed to the scattering of the collected Raman signals. The laser intensity was kept at a low level to minimise heating of the hydrate samples, which led to a low signal-to-noise level. Defects existed on the surface and the surface morphology changed during the exchange process, in particular on the outer surface of the particle. The morphology and transparency of the hydrate sample had a substantial impact on both the incident laser and scattered Raman signals.

Despite these effects on scattered signal intensities, normalised Raman measurements can provide an estimate of the gas diffusion coefficient. Raman intensity is known to inflate with increasing temperature so the Raman response of CO₂ and CH₄ hydrates was normalised to the intensity of the OH vibration at 3020 cm^{-1} . The ratio was tested in baseline studies and remained steady over the experimental temperature range. The change of this ratio with time was interpreted assuming Fick's second law and a one-dimensional diffusion process in order to extract an effective diffusion coefficient (D_e). Figure 6.12 illustrates the measured concentrations of CO₂ hydrates and the calculated concentrations of CO₂ hydrates, assuming a simple diffusion process.

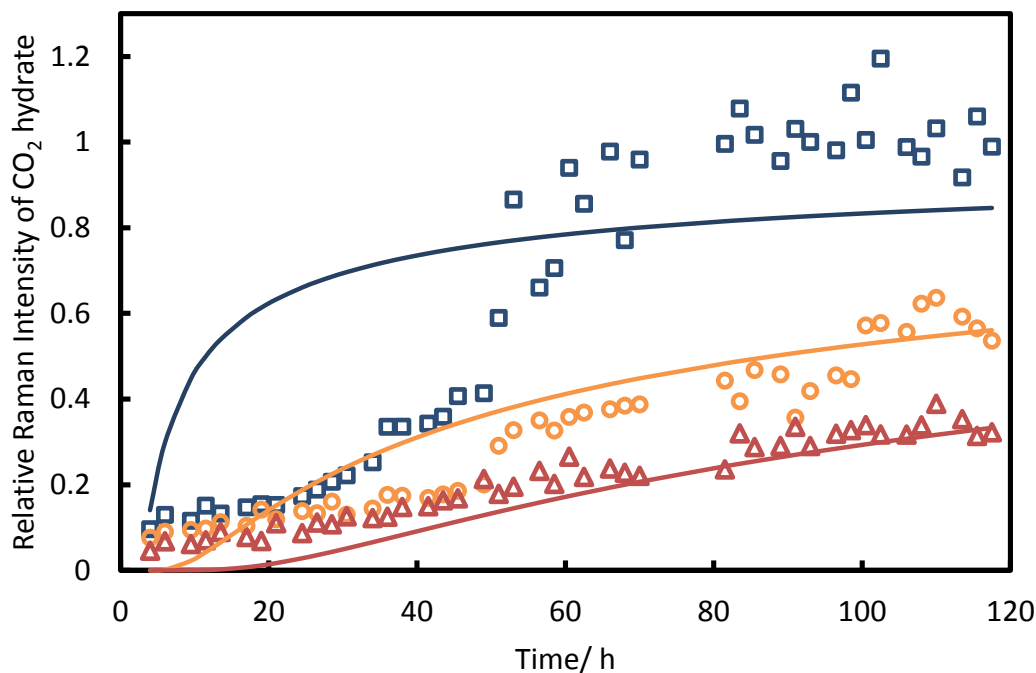


Figure 6.12 Relative intensities of CO_2 hydrates over OH bond, assuming $D_e = 8 \times 10^{-16} \text{ m}^2/\text{s}$ (Lengths indicate distances from the edge of the particle); $\square$, CO_2 hydrates at $5 \mu\text{m}$; $\circ$, CO_2 hydrates at $15 \mu\text{m}$; $\triangle$, CO_2 hydrates at $25 \mu\text{m}$; —, Calculated CO_2 hydrates at $5 \mu\text{m}$; —, Calculated CO_2 hydrates at $15 \mu\text{m}$; —, Calculated CO_2 hydrates at $25 \mu\text{m}$.

An average diffusion coefficient was used and assumed to be $8 \times 10^{-16} \text{ m}^2/\text{s}$. Such a simple estimate of the diffusion coefficient (see Figure 6.12) was unable to cover (i) variations of the diffusion coefficient with the increasing temperatures, and (ii) intrinsic kinetics of the gas exchange. At low temperatures where the thermal driving force of the exchange was relatively small, the intrinsic kinetics of exchanging a CO_2 molecule for a CH_4 molecule within a hydrogen-bonded water cage also play a critical role in the overall exchange rate. It is hard to segregate contributions from the exchange kinetics and the diffusion process. However the estimated overall diffusion coefficient is in good agreement with earlier studies of the solid diffusion process in gas hydrate systems in a range 1×10^{-16} to $2 \times 10^{-14} \text{ m}^2/\text{s}$ [204-206].

6.6.3 Three-dimensional Raman Imaging of CH_4 Hydrates

The Raman imaging technique takes advantage of a high-resolution line focus Raman system and a motorised microscope stage. Unlike the point focusing approach, the laser was split into a line using a cylindrical lens; the scattered Raman signal was also detected from the same area and this was scanned across a plane through the sample to give a 2D image in about 19 minutes across an area of $510\text{ }\mu\text{m}$ by $510\text{ }\mu\text{m}$. A 3D image was built up by moving the stage vertically in an increment of $65\text{ }\mu\text{m}$ to scan successive planes. The line focusing technique sacrificed signal intensity, which was reduced by a factor of 10 compared with the single point method, for an acquisition time. The Raman imaging technique facilitated the study of rapid rate processes and greatly reduced the acquisition time (up to a few hours in the same area) from customary point-by-point Raman mapping methods. Figure 6.13 shows the Raman imaging of methane hydrates at different depths.

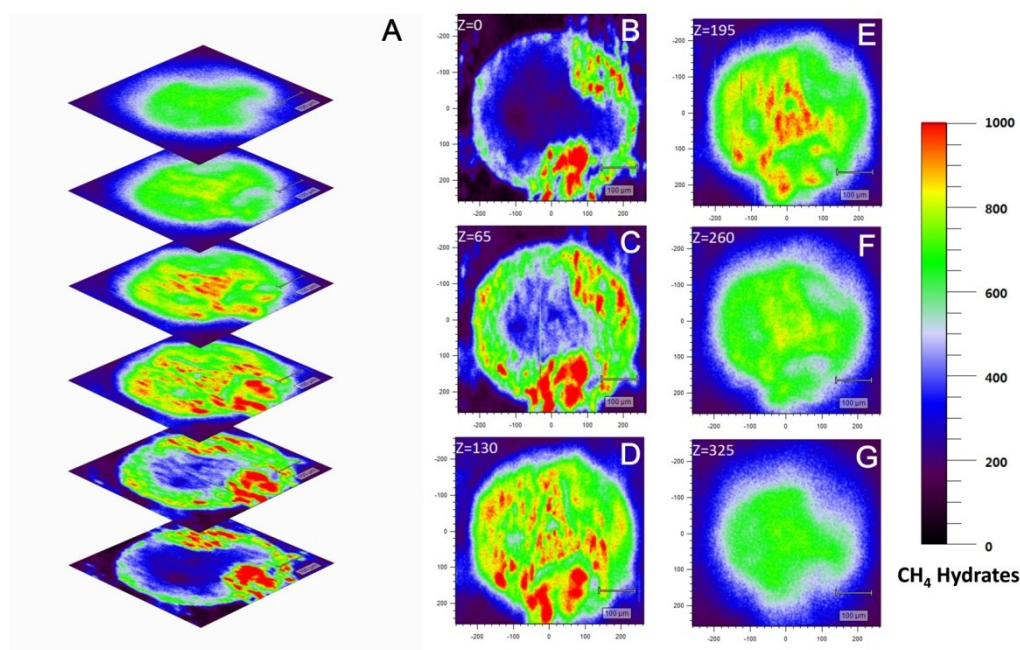


Figure 6.13 Three-dimensional geometry of CH_4 hydrates; A, Stacking Pictures of Raman images; B, C, D, E, F, and G, Raman images at $0\text{ }\mu\text{m}$, $65\text{ }\mu\text{m}$, $130\text{ }\mu\text{m}$, $195\text{ }\mu\text{m}$, $260\text{ }\mu\text{m}$, and $325\text{ }\mu\text{m}$ from the bottom of the hydrate particle. Raman images were acquired at 4.1 MPa and 273.65 K . The polycrystalline methane hydrates grew using the temperature oscillation method under large thermal driving force .

The cross-sections of three-dimensional images show the Raman intensity at different location within the hydrate particle. The hydrate particle has a diameter about 450 μm . Since these methane hydrate particles are semi-transparent, the incident laser at 532 nm could not penetrate fully into the core of the sample due to excessive scattering from defects with depth; the Raman signal intensity dropped significantly near the core of the hydrate particle. The Raman images illustrate visually the shape of the hydrate particle and also quantitatively map out the location and spatial distribution of methane hydrate. Unlike single point measurements, Raman images visualise the heterogeneity of a hydrate particle. Since it takes many hours to fully form methane hydrates or to exchange the methane guest molecules for other gases such as CO₂, streamline Raman Imaging could potentially be used to study the kinetics of hydrate formation and exchange. More generally, this new high pressure, controlled temperature Raman cell opens up many possibilities for the study of the spatial distribution of material composition and structure, and their temporal variations.

6.6.4 Raman Imaging of Hydrates with Different Morphologies

Under different conditions, methane hydrates with different morphologies were formed (see Figure 6.14). To the author's knowledge, single crystal methane hydrates were formed for the first time* in a vapour environment via a controlled formation method. Single crystal methane hydrates (Figure 6.14a) showed complete transparency and exhibited hexagonal prism shape. Semi-transparent methane hydrates (Figure 6.14b, c, and d) with irregular shapes were partially transparent and had defects on the surface. The polycrystalline hydrates were opaque. The polycrystalline hydrate particles maintained the shape of the original water droplets, and some branches were extended from the original hemispherical shape. When the surface of a polycrystalline hydrate particle was focused in the microscope, local bright points were observed, indicating the existence of small crystal grains locally.

* Single crystal methane hydrates were previously formed in aqueous environments under ultra-high pressures [28, 32, 33]. Such crystals are not suitable for gas exchange studies due to the pressure media and the geometry of the cell.

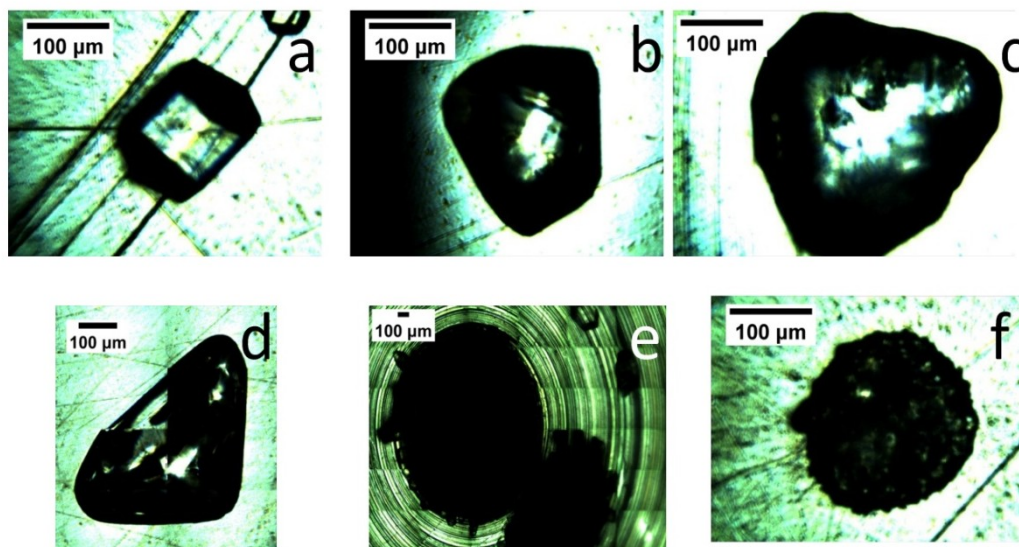


Figure 6.14 Morphologies of methane hydrate crystals grown under different conditions (a) transparent hexagonal single crystal methane hydrates grown at 14 MPa and 286.1K; (b), (c) and (d) semi-transparent single crystal methane hydrates grown at 14 MPa with 5 to 15 K driving force, (e) and (f) Polycrystalline methane hydrates grow using the temperature oscillation method under large thermal driving force. Scale bars indicate 100 μm in length.

The heterogeneity of different hydrate crystals was illustrated by Raman images that were reconstructed from Raman signals of CH_4 hydrate in large cages at 2906 cm^{-1} (see Figure 6.15). The transparent single crystal methane hydrates showed uniform Raman responses and relatively high Raman intensities (Figure 6.15a), whereas polycrystalline methane hydrates (Figure 6.15e and Figure 6.15f) had strong Raman responses only around the edge of the hydrate particles. Due to the low transparency of the polycrystalline hydrates, the incident laser and scattered Raman signals had difficulty in penetrating through the upper hydrate layer, leading to low Raman intensities in the middle of the focal plane. Defects and uneven surfaces with reduced Raman intensities on the semi-transparent hydrate particles were also indicated by Raman images (Figure 6.15 b, c, and d).

It was also found that the intensity of the lattice vibration mode of CH_4 hydrates was sensitive to the crystal morphologies. The Raman intensity of the lattice vibration from single crystals was significantly stronger than that from polycrystalline hydrates. Due to the lack of proper calibration standards, quantitative measurements were not conducted to compare the lattice vibration signal from single crystal methane hydrates and polycrystalline methane hydrates.

The Raman intensity was also sensitive to the height of the focal plane for semi-transparent and polycrystalline hydrates. The defects and crystalline boundaries acted as signal barriers. Hence, at different heights, CH_4 hydrates showed different Raman intensities. The Raman imaging technique is a valuable technological advance compared to single point Raman measurements in being able to detect and illustrate heterogeneities of materials.

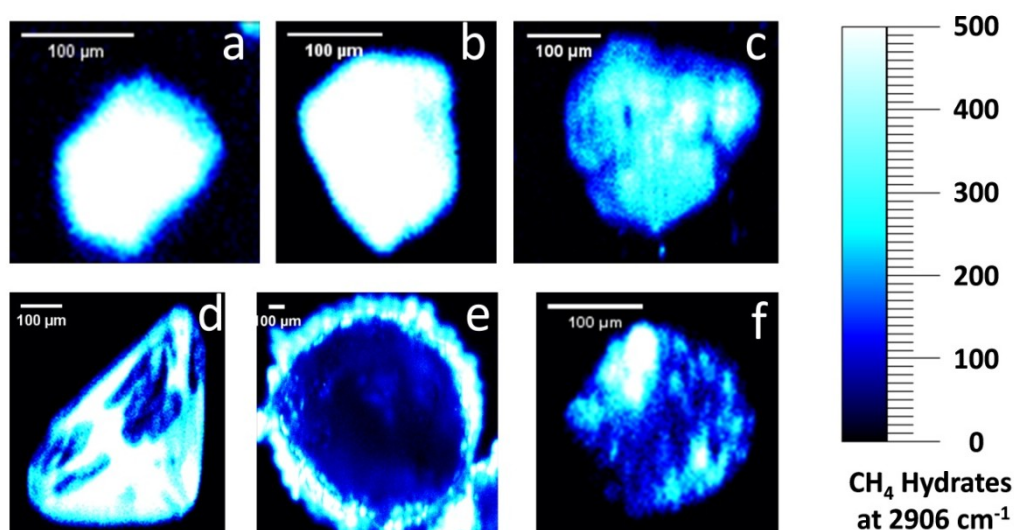


Figure 6.15 Raman imaging of different hydrate crystals at 273.65 K and 3 MPa. (a) transparent single crystal methane hydrates; (b), (c) and (d) semi-transparent single crystal methane hydrates with defects, (e) and (f) Polycrystalline methane hydrates. Colour scale indicates the Raman intensity (peak height) of methane hydrate at 2906 cm^{-1} . 10 mW laser power and 3.24 s exposure time were used for all images except for (e) where 50 mW laser power and 1.72s exposure time were used. Scale bars indicate 100 μm in length.

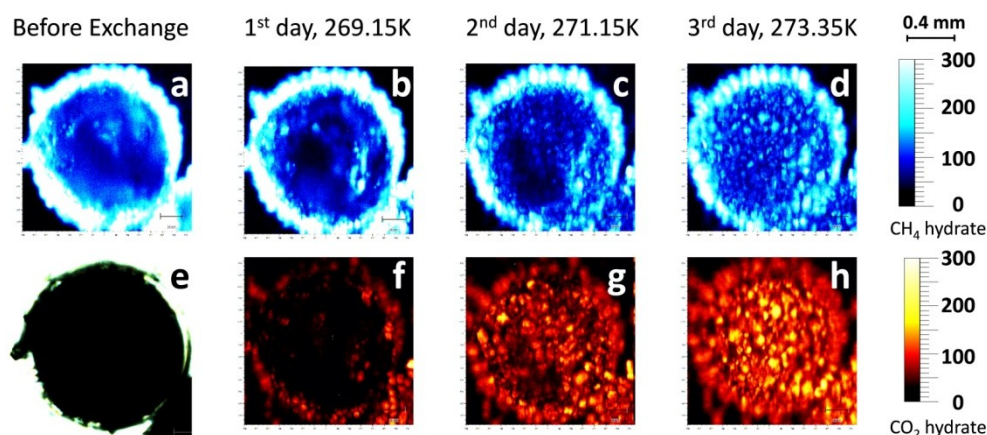
6.6.5 Raman Imaging of $\text{CH}_4\text{-CO}_2$ Exchange - Polycrystalline Hydrates

Figure 6.16 Exchange Experiment 1: Raman Mapping of a three-day exchange experiment at 3 MPa for polycrystalline CH_4 Hydrates at 2906 cm^{-1} (a, b, c, and d), being replaced by CO_2 Hydrates at 1381 cm^{-1} (f, g, and h) and an initial white light Image (e). The temperature was increased every 24 hours as indicated. Images were scanned at $260\text{ }\mu\text{m}$ above the silver substrate surface. The height of the droplet was around $500\text{ }\mu\text{m}$. 50 mW Laser power and 1.72 s exposure time were used.

Amorphous (polycrystalline) CH_4 hydrates were formed under large thermal driving forces. Under such conditions, a high degree of misalignment and disorder of the lattice structure was expected to exist. The grain boundaries of the small crystals in the polycrystalline hydrates facilitated the diffusion process of CO_2 molecules into the solids and provided high gas-solid contact surface area for the three-day exchange process, during which CO_2 hydrates initially formed around the edge of the amorphous hydrate particle (see Figure 6.16f). As the exchange process progressed, CO_2 hydrates evolved deeper into the hydrate particle (see Figure 6.16g and h). At 273.35 K, a multitude of CO_2 hydrate regions developed throughout the hydrate particle, leading to a mixed $\text{CH}_4\text{-CO}_2$ hydrate. When the temperature was raised from 271.15 K to 273.35 K at 3 MPa, partial dissociation of methane hydrates was observed due to a decrease of CH_4 hydrate's stability as the temperature moved above its melting point at this pressure. The dissociation of methane hydrates accelerated the exchange process and provided free water in the system. Newly formed $\text{CH}_4\text{-CO}_2$ hydrates were also found on free surfaces of the cell. Another five-day exchange experiment led to similar conclusions (see Experiment 6 in section 6.67).

6.6.6 Raman Imaging of $\text{CH}_4\text{-CO}_2$ Exchange – Semi-transparent Hydrates

Two semi-transparent hydrate particles were formed separately. The original hexagonal or tetragonal shape was disturbed by different growth rates on different faces. Defects and dislocations reduced the transparency of the crystals; both white light images and Raman images of the CH_4 hydrate particles suggested the existence of defects in the hydrate particle.

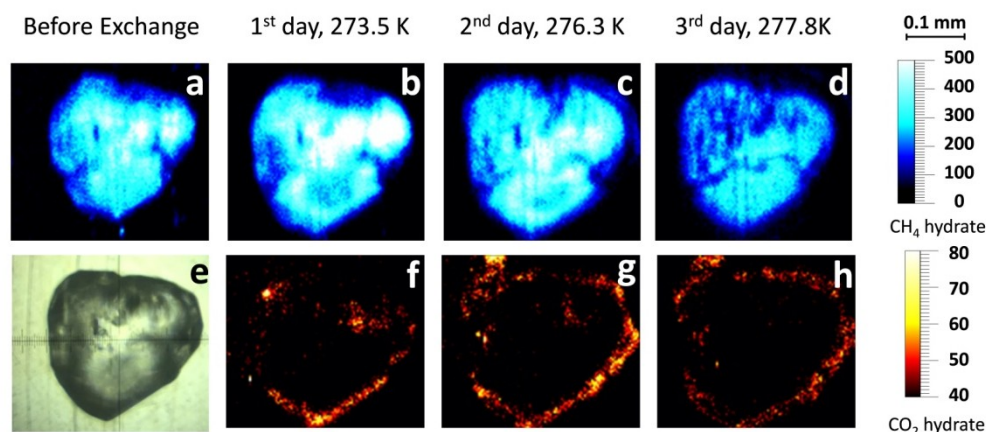


Figure 6.17 Exchange Experiment 2: Raman Mapping of semi-transparent CH_4 Hydrates at 2906 cm^{-1} (a, b, c, and d), and CO_2 Hydrates at 1381 cm^{-1} (f, g, and h) with the white light Image (e) during a three-day exchange experiment at 3 MPa. The temperature was increased every 24 hours, as indicated.

Semi-transparent crystals exhibited a slower exchange rate in comparison with polycrystalline hydrates. A three-day exchange experiment was performed initially (see Figure 6.17). During the exchange process, the intensity of CH_4 hydrates gradually decreased. The reduction of CH_4 signal intensity was particularly distinct on the edge of the hydrate particles and at locations with defects (defects were located by dark spots in white light images, see Figure 6.17e). CO_2 hydrates slowly emerged on the brink of the hydrate particles and around some sites with defects during the exchange process. In contrast with polycrystalline hydrates, the exchange process with a semi-transparent crystal only occurred on the edge of the hydrate crystal and was greatly limited by the diffusion of CO_2 molecules into the hydrate crystal. A slight decrease of CO_2 hydrate intensity was observed on Day 3 when the temperature was raised from 276.30 K to 277.80 K, at which CH_4 hydrates became unstable. Such a temperature might cause partial dissociation of mixed $\text{CH}_4\text{-CO}_2$ hydrates, leading to the

decreased intensity of CO_2 hydrates. Similar phenomena were observed during a five-day exchange experiment with another semi-transparent crystal (see Figure 6.18).

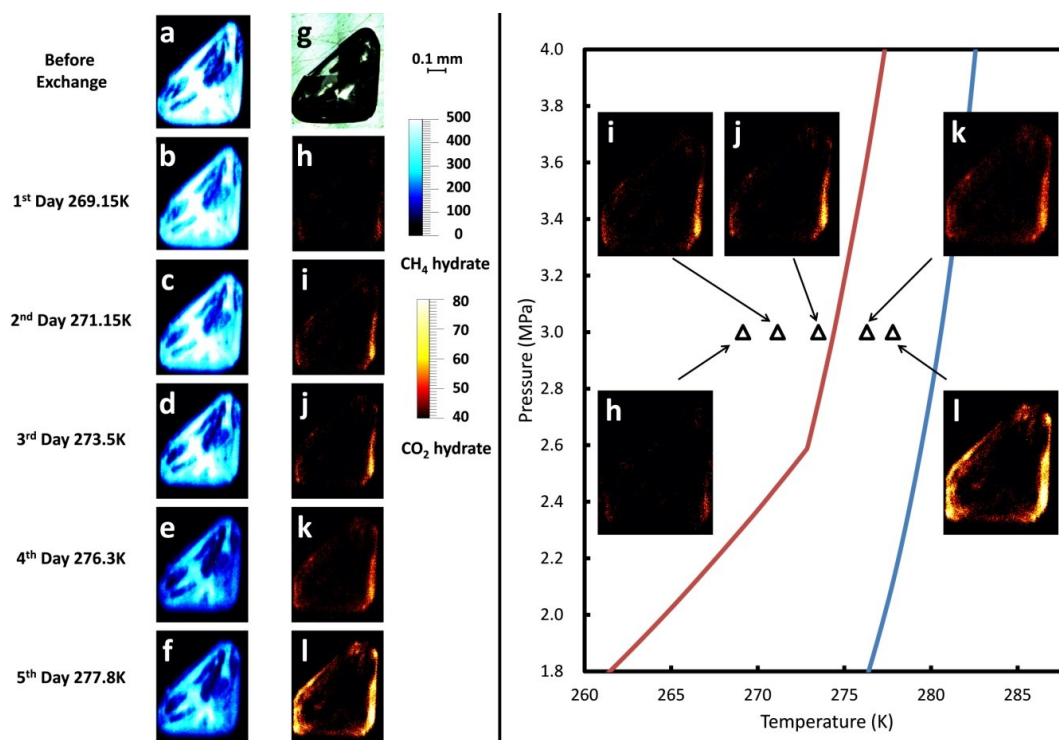


Figure 6.18 Exchange Experiment 3: Raman Mapping of semi-transparent CH_4 Hydrates at 2906 cm^{-1} (a, b, c, d, e, and f), and CO_2 Hydrates at 1381 cm^{-1} (h, i, j, k, and l), with the initial white-light Image (g); Δ , Temperature-pressure conditions during the exchange; —, Phase diagram of CH_4 hydrates (unstable to the right); —, Phase diagram of CO_2 hydrates (unstable to the right);

Here the exchange rate was mainly controlled by the temperature-pressure conditions. As the first layer of CO_2 hydrates formed, the exchange process showed the characteristics of a gas-solid diffusion process. At 269.15 K and 271.15 K (see Figure 6.18h and Figure 6.18i), the exchange process was relatively slow, limited by both a slow gas diffusion rate and the small kinetic driving forces at these lower temperatures. When the temperature was ramped to 273.50 K (Figure 6.18j) and 276.30 K (Figure 6.18k), CO_2 hydrate covered a larger area around the edge of the semi-transparent hydrates. However, a slight decrease in the Raman intensity of CO_2 hydrates was observed, which might be attributed to the decreased stability of CH_4 hydrates under such conditions. Large amounts of CO_2 hydrates were found on the 5th day (Figure 6.18l) when the kinetics were more favourable for the CO_2 replacement process and CH_4 hydrate is thermodynamically unstable. The three-dimensional distributions of the

CH_4 and CO_2 hydrates are demonstrated by vertically stacking Raman images scanned at different heights (see Figure 6.19), which shows that the CO_2 hydrates were unevenly distributed around the perimeter layer of the hydrate crystal.

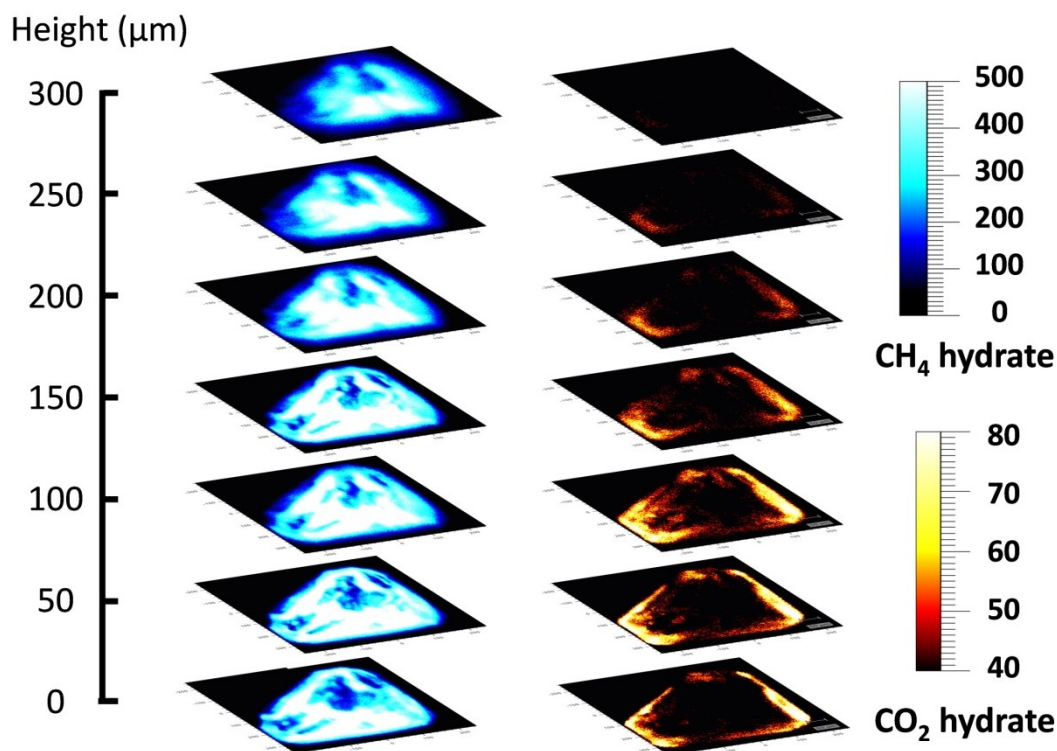


Figure 6.19 Raman Mapping of semi-transparent CH_4 Hydrates at 2906 cm^{-1} , and CO_2 Hydrates at 1381 cm^{-1} by the end of Experiment 3 ($t = 5$ days) at 3 MPa. Height indicates the distance of the scanning plane from the bottom of the semi-transparent hydrate crystal.

CO_2 hydrates formed in the interior of the crystal were located preferentially near the defect sites of the original methane hydrate crystal. It is possible that these defects facilitated the exchange process by either providing higher conductive pathways for gas diffusion within the solid crystal or providing greater local free volume to enable the re-arrangement of the hydrate cage structure, which would be necessary to enable CH_4 to be replaced by CO_2 , to take place more easily. During two exchange experiments with semi-transparent hydrates (Experiments 2 and 3), the thickness of the CO_2 hydrate perimeter layer was around $50\text{ }\mu\text{m}$ in both experiments, with some variations due to the morphology and geometry of the hydrate particles. However, the thickness of the CO_2 hydrate layer was predominately determined by the duration of the experiments and the temperature-pressure conditions at which the

exchange experiments were conducted. During the exchange process, the CO₂ hydrate layer reduced the transparency of the semi-transparent crystal, maybe reflecting the destruction and reconstruction of the hydrate lattice structure.

6.6.7 Raman Imaging of CH₄-CO₂ Exchange - Transparent Single Crystal Hydrates

The changes observed during CH₄-CO₂ gas exchange for the single crystal hydrates are shown in Figure 6.20. Both the white light images and Raman images suggest that the shape of the methane hydrate crystal remained intact throughout the exchange process, with only a slight decrease in transparency. The reduction in transparency became noticeable at 276.30 K. The flat surface at the centre of the crystal revealed pronounced Raman intensities, whereas, in comparison, rather weak Raman intensities were observed on the side facets from which partially diffracted Raman signals were expected. The variation in the Raman intensity for the CH₄ hydrates was mainly caused by the changes in temperature. During the exchange process, the temperature rise led to an increase in Raman intensities and the CO₂ substitution could contribute to a decrease in CH₄ Raman response. The temperature-driven variations in Raman intensities were less than 9 % of the CH₄ Raman intensities at 269.15 K (based on previous calibrations under the same experimental conditions). The decomposition and substitution of CH₄ hydrates should have a notable impact on the intensities of the CH₄ hydrate image. However, no conspicuous exchange was detected during the experiment. A slight decrease of CH₄ hydrate signal was observed at 276.30 K and 277.80 K, which was consistent with the slight amount of CO₂ hydrates recorded during the exchange process (see Figure 6.20r). The slow exchange rate observed with transparent crystal hydrates indicated that the lattice (volume) diffusion of CO₂ molecules into the perfect crystal was extremely slow. The perfectly ordered crystal lattice acted as a strong diffusion barrier which prevented CO₂ molecules from interacting with CH₄ hydrates and replacing CH₄ molecules in the cages. It is also possible that the highly constrained water cages of the hydrate were unable to re-arrange sufficiently on the timescale of these experiments to enable the substitution of many CH₄ molecules by CO₂, despite the greater thermodynamic stability of the CO₂ hydrates.

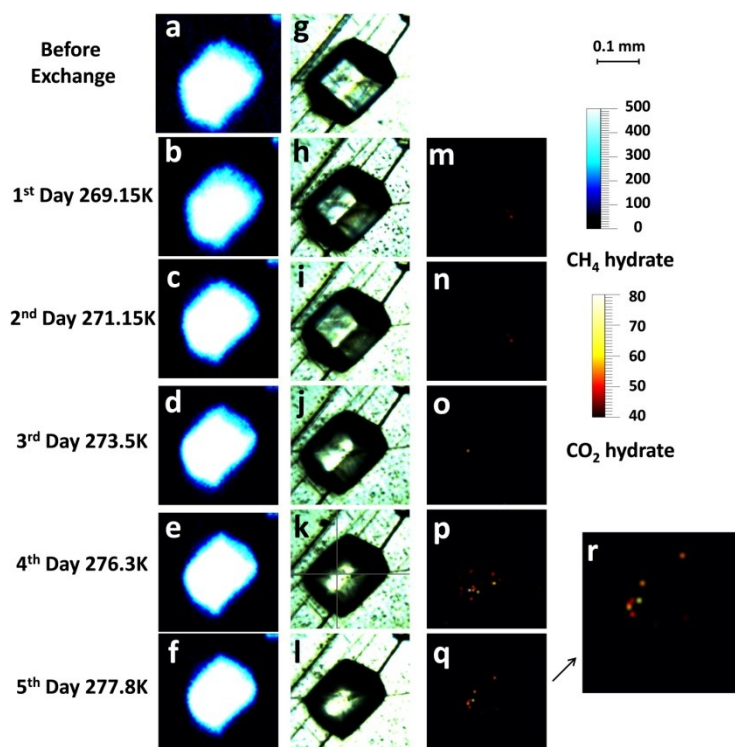


Figure 6.20 Exchange Experiment 4: Raman Mapping of single crystal CH_4 Hydrates at 2906 cm^{-1} (a, b, c, d, e, and f), CO_2 Hydrates at 1381 cm^{-1} (m, n, o, p, and q) and expanded view of q (r) with white-light images (g, h, i, j, k, and l). The temperature was increased every 24 hours as indicated.

6.6.8 Comparison of $\text{CH}_4\text{-CO}_2$ Exchange from Different Morphologies

The images of three CH_4 hydrate particles with different morphologies under identical experimental conditions are compared in Figure 6.21 and Figure 6.22. The CH_4 polycrystalline hydrate and the CH_4 single crystal hydrate in fact coexisted in the same experiment (Raman images from the first two days, during which CO_2 hydrate signal from the transparent single crystals was negligible, are not shown.). These figures clearly demonstrate the major effect the crystal morphology has on the gas exchange rate.

Due to the existence of the grain-boundaries in polycrystalline hydrates, CO_2 molecules penetrated readily into the inner part of such particles, with CO_2 hydrate being present across 55% of the image cross-section within 72 hours and across 95 % in 120 hours. In contrast, the extended stability of the transparent CH_4 hydrate single crystal might be attributed to a much slower lattice diffusion process compared to a faster grain-boundary diffusion process in the polycrystalline hydrates. Only trace amounts of CO_2 hydrates, present in less than 1 % of the

single crystal cross-section after 120 hours, were detected on the top surface of the hydrate crystal. The CO_2 hydrate signal from the side facets was possibly weakened by diffraction. Such a thin layer of weak CO_2 hydrate signal was below the detection limit of the Raman system.

Semi-transparent hydrate crystals exhibited an intermediate exchange rate compared to the transparent crystals and polycrystalline hydrates. CO_2 replacement occurred on the surface of the particles and preferentially around locations with defects, where grain-boundaries were likely to exist. The grain-boundaries accelerated the diffusion of CO_2 molecules into the hydrate crystal and also increased the reactive surface area for the $\text{CH}_4\text{-CO}_2$ exchange process.

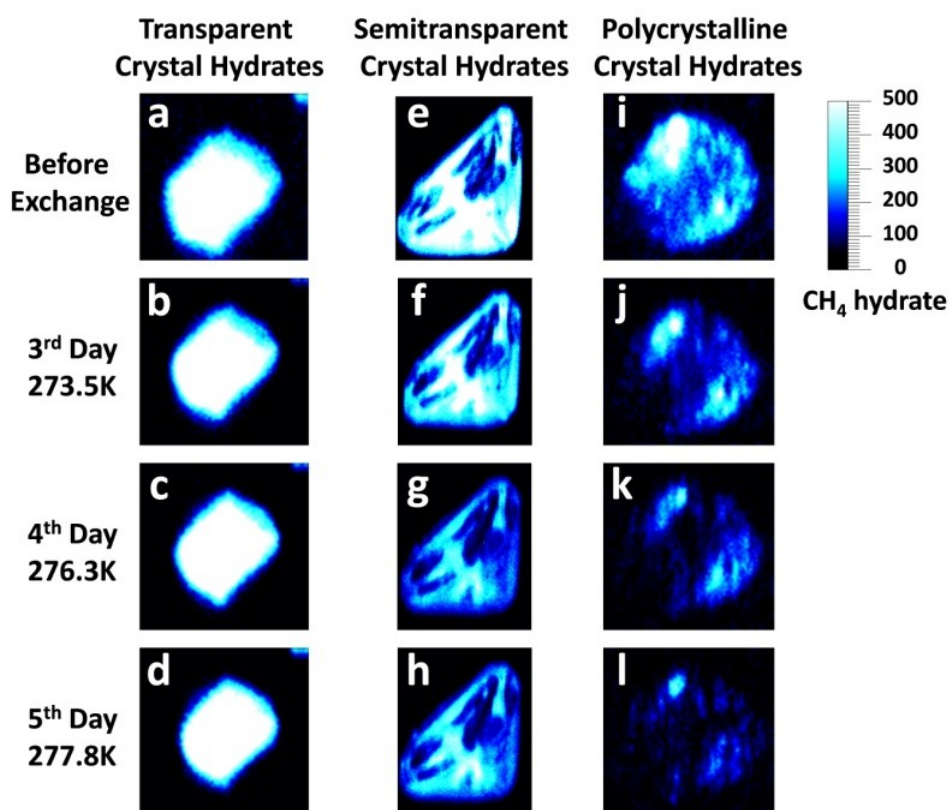


Figure 6.21 Comparison of Raman images of CH_4 hydrates at 2906 cm^{-1} during a five-day exchange experiment for crystal hydrate (a, b, c, and d – Experiment 4), semi-transparent crystal hydrates (e, f, g, and h - Experiment 3) and polycrystalline hydrates (i, j, k, and l – Experiment 6).

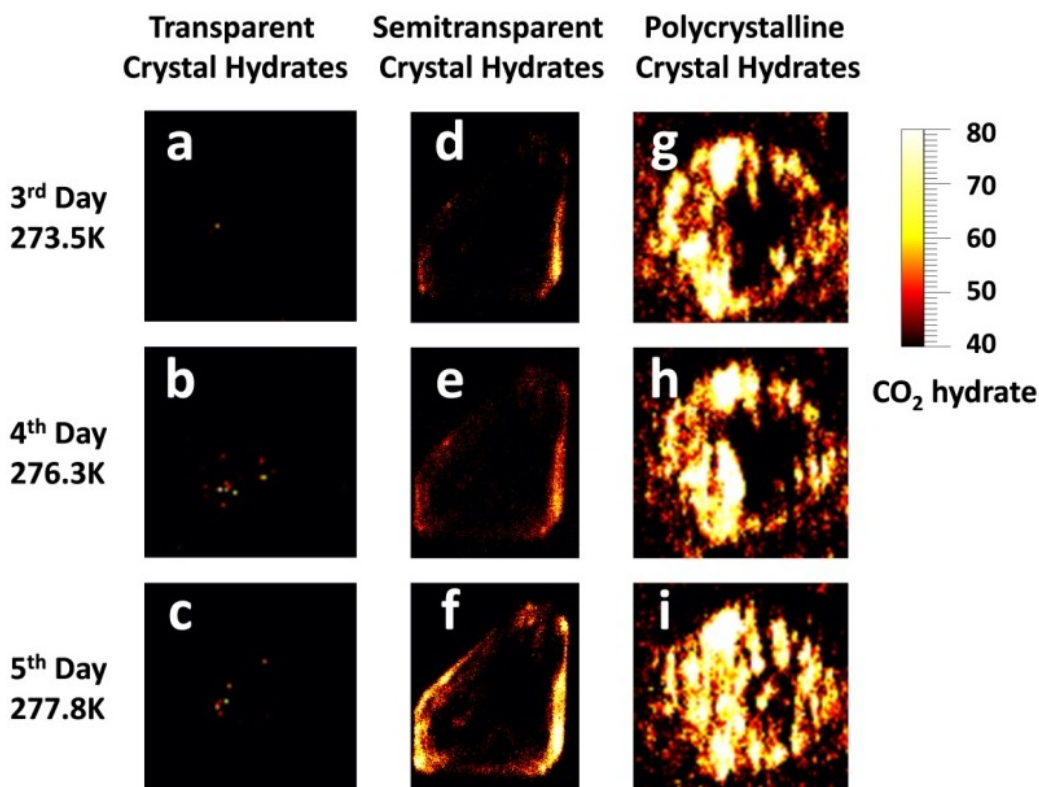


Figure 6.22 Comparison of Raman images of CO₂ hydrates at 1381 cm⁻¹ during a five-day exchange experiment for crystal hydrate (a, b, and c - Experiment 4), semi-transparent crystal hydrates (d, e, and f – Experiment 3) and polycrystalline hydrates (g, h, and I – Experiment 6).

6.7 Summary

In this chapter, *in-situ* measurements of the replacement of methane by carbon dioxide in hydrate crystals were carried out using confocal Raman spectroscopy with a rapid imaging capability. The acquisition of Raman images capturing the extent of CH₄-CO₂ exchange in 300 μm by 300 μm samples with a spatial resolution better than 2 μm required only 15 minutes. Single point measurements were also conducted to monitor cage occupancies and determine the diffusion coefficient of CO₂ into methane hydrates during the exchange process.

Guest exchange was studied in three types of hydrate crystal morphology. Polycrystalline hydrates were synthesised on hydrophobic surfaces by oscillating the temperature between 278.15 K and 248.15 K with a ramp rate of 3 K·min⁻¹ under 15 MPa of methane. Full conversion of all the water present into hydrate occurred in 24 hours. In contrast, single crystal methane hydrates were formed isothermally at 14 MPa by using a small thermal

driving force (ca. 3 K) from deionised water droplets (0.02 μ L each). These crystals normally grew over a 24 hour period although the induction time varied from minutes to several hours. Single crystal methane hydrates exhibited a hexagonal prism shape and were transparent under the visual microscope. In some cases, defects were intentionally introduced into the single crystal methane hydrates by increasing the temperature driving force applied to 5 K at 14 MPa, which resulted in a third, semi-transparent hydrate morphology.

Following the formation of a given hydrate crystal morphology, the CH₄ atmosphere was replaced by pure CO₂ at 3 MPa and 269.15 K. The temperature was kept constant for 24 hours at each of the set points (269.15 K, 271.15 K, 273.50 K, 276.30 K, and 288.80 K) before being ramped to the next temperature. State-of-the-art Raman Spectral Imaging was then used to study the CH₄-CO₂ exchange kinetics in representative samples of single crystal, semi-transparent, and polycrystalline methane hydrates. Raman images of CO₂ hydrates and CH₄ were acquired every 8 hours, and 10 point measurements across the sample were conducted every 30 minutes.

Results from single point measurements of semi-transparent hydrates show that the relative occupancy (θ_L/θ_s) of CH₄ in the large ($5^{12}6^2$) and small (5^{12}) hydrate cavities decreased as exchange progressed. Relative CH₄ occupancy was determined from the enclathrated CH₄ ν_1 symmetric stretching peaks at 2906 cm^{-1} and 2917 cm^{-1} and changed from 3.12 (before exchange) to 1.15 (after exchange). While the relative CO₂ cage occupancy cannot be resolved from its Raman spectra, the intensity of the enclathrated CO₂ signal increased as the CH₄ relative occupancy decreased, suggesting that the CO₂ molecules preferentially occupied the large $5^{12}6^2$ hydrate cages. The Raman Imaging results revealed different exchange behaviour in each hydrate morphology. Due to the inherent porous structure of the polycrystalline hydrates, CO₂ molecules penetrated readily into the inner part of such particles, with CO₂ hydrate being present across 55% of the polycrystalline cross-section within 72 hours, and across 95 % in 120 hours. In contrast, the single crystal methane hydrates showed an extended stability during the exchange, with CO₂ hydrates being present across less than 1 % of the single crystal cross-section after 120 hours. The shape of the single crystal methane

hydrates remained intact with only a slight decrease in transparency. The Raman images and spot measurements both showed that the penetration depth of CO₂ into the semi-transparent methane hydrates during a 5 day experiment was around 50 μm , which allows a simple estimate of $8 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ to be made for the diffusion coefficient of CO₂ into these crystalline solid hydrates. Overall, the results suggest that CH₄-CO₂ exchange initiates and propagates from either the surface or via internal defects such as grain boundaries in methane hydrate crystals (facilitating hydrate cage re-arrangement and faster diffusions) and that the detailed crystal morphology plays a critical role in determining the overall rate of the gas exchange process. Diffusion alone does not appear to be the sole limiting factor in the extent and rate of gas exchange in solid hydrates, with the availability of sufficient local free volume to enable the local rearrangement of the hydrogen-bonded water cage lattice (partial local melting) a probable key factor in the exchange mechanism.

The techniques developed in this work have enabled a detailed quantitative characterisation of the spatial and temporal composition changes during gas exchange in CH₄-CO₂ hydrates. The results provide cogent evidence for how the initial morphology of the hydrate crystal affects the rate and degree of CH₄-CO₂ exchange, which probably explains some of the large discrepancies reported in the literature for CH₄-CO₂ exchange measurements [184-188]. Clearly, characterising the nature of the crystal morphology present in any naturally occurring hydrate sediment will be crucial for knowing the likely exchange rate and for the design of simultaneous CO₂ sequestration and CH₄ recovery processes.

Chapter 7

Conclusions and Recommendations for Future Work

7.1 Conclusions

In this work, the goal is to develop a better understanding of gas hydrates under conditions relevant to natural gas hydrate systems and their potential exploitation. This knowledge can ultimately lead to feasible field production/exploration methods or better management of gas hydrates during gas transportation and separation. Three pieces of apparatus were used in this work: a stirred high-pressure low-temperature autoclave reactor—working isothermally and isobarically—was used to study the formation kinetics of methane hydrates under various driving forces and water-based media; a high-pressure differential scanning micro-calorimetry was used to measure thermophysical properties of gas hydrates in confinement and in bulk; and a piece of high-pressure Raman apparatus with *in-situ* Raman imaging capabilities was devised to study the exchange kinetics of methane hydrates with carbon dioxide under reservoir conditions.

New experimental data related to the formation kinetics of methane hydrates have been collected at temperatures between 276.5 K and 283.5 K and pressures between 5 MPa and 10.5 MPa with a focus on (a) the effect of the available gas-water interfacial area for mass transfer and reaction during gas hydrate formation, (b) the effect of the driving force, and (c) the physical state of the water phase from which hydrate is formed. The formation rate of methane hydrates in an agitated binary methane and water system showed a strong dependency on the hydrodynamic conditions, such as the gas-liquid interfacial area, the degree of mixing and gas entrainment. The formation rates of methane hydrates followed a simple approximately exponential trend with the chemical potential difference from the equilibrium state for different (P , T) conditions. Such a dependency suggests that the displacement from the equilibrium conditions, regarded as a driving force of the hydrate

formation (i.e., chemical potential difference), determines the initial formation rates of methane hydrates. An empirical polynomial model was proposed to correlate the formation rate of methane hydrates and chemical potential difference to within $\pm 5\%$.

The hydrate formation rate was also studied for a methane-micronised ice particle system and a methane-‘Dry Water’ system, which have increased water surface areas of $300.9\text{ cm}^2\cdot\text{g}^{-1}$ and $16800\text{ cm}^2\cdot\text{g}^{-1}$, respectively, compared to that of the stirred water system ($1.0\text{ cm}^2\cdot\text{g}^{-1}$). The results indicated that large differences in the reactive surface area and gas diffusion rates for these three different precursor systems resulted in pronounced effects on the initial formation rate of methane hydrates. The fastest apparent formation rate of methane hydrates was obtained from the Dry Water system, which showed a tenfold increase in the formation rates without any agitation compared with those from stirred water system. The fast formation rate in the Dry Water system was likely caused by the presence of silica particles, which acted as heterogeneous nucleation sites at the liquid-gas interface, as well as the increased available surface area for gas-water mass transfer. Comparing the formation rate of methane hydrates in the stirred water system and the Dry Water system, the net increase in the formation rate (ca. 10 times) was much smaller than the increase in the surface area (ca. 300 times), suggesting that the coverage of silica particles at the interface might reduce the available surface area for the hydrate formation. Comparing the increase in the surface area and in the formation rate gave a simple estimate of the surface coverage ratio of silica particles in the Dry Water system of 94.1%. Therefore only about 6% of the water droplet surface area was available for gas-water mass transfer. The slowest formation rate of methane hydrates was observed in the ice system, which was around 10 times smaller than that from the stirred water system, despite the large surface area ($16800\text{ cm}^2\cdot\text{g}^{-1}$) generated by the micronised ice particles. The reduced formation rate in the ice system was likely caused by a slow nucleation process at the gas-solid interface in comparison with the liquid-gas interface in the stirred water system and the heterogeneous solid-liquid-gas interface in the Dry Water system and slow diffusion of methane through the hydrate layer formed on the surface of the ice particles and into the ice core.

In the study designed to investigate the melting behaviour of natural gas hydrates, which are usually formed in porous mineral sediments rather than in bulk, hydrate phase equilibria for binary methane and water mixtures have been studied using high-pressure differential scanning micro-calorimetry in mesoporous and macroporous silica particles at pressures up to 50 MPa. These particles have controlled pore sizes that range 8.5 nm to 195.7 nm. A dynamic oscillating temperature method was used to fully convert the ice/water pre-cursor into hydrates reproducibly and then determine their decomposition behaviour—melting points and enthalpies of melting. For a given surface chemistry (here silica), the melting points of methane hydrates are depressed by confinement in micropores in a way that is consistent with the Gibbs-Thomson equation. This reduction depends linearly on the reciprocal of the pore radius. This phenomenon can lead to a reduction of 5 K or more for pores of ~10 nm diameter. Furthermore, it was observed for the first time that this effect shows a marked (essentially logarithmic) dependence on pressure, which has been ascribed here to the known variation of interfacial tension with pressure. An empirical modification of the Gibbs-Thomson Equation has been adopted to include this effect. The effects of interfacial energy on the confined phase equilibria were further investigated by functionalising the pores of the silica particles to change the pore surface chemistry. The confinement effect on gas hydrate melting is promoted by hydrophilic surfaces and inhibited by hydrophobic pores; methane hydrates in hydrophobic porous silica demonstrated melting behaviour, which is essentially the same as bulk hydrates, indicating negligible interaction with the pore surface of the hydrogen-bonded hydrate cage structure.

In order to investigate the hydrate guest molecule composition and spatial distribution, a high-pressure low-temperature optical reactor was designed, commissioned and applied for Raman spectroscopy and imaging studies of multiphase systems. This can be used for crystalline solids and soft materials under extreme conditions, including gas hydrates at high pressures and low temperatures. The cell enabled samples to be analysed over a temperature range of 288 K to 353 K and at pressures up to 50 MPa. Fast temperature response (up to 5 K·s⁻¹), and stable temperature control (± 20 mK) were facilitated by using four Peltier elements. A large optical path allowed the acquisition of *in-situ* 3D Raman images to reveal

the molecular structure and (CH₄-CO₂) exchange kinetics of gas hydrates in three different types of hydrate crystal morphology.

Polycrystalline hydrates were synthesised on hydrophobic surfaces by oscillating the temperature between 278.15 K and 248.15 K at a ramp rate of 3 K·min⁻¹, and under 15 MPa of methane. Full conversion of all the water present into hydrate occurred in 24 hours. In contrast, single crystal methane hydrates were formed isothermally at 14 MPa by using a small driving force (ca. 3K) from small deionised water droplets (0.02 µL each). Single crystal methane hydrates exhibited a hexagonal prism shape and were transparent under the visual microscope. In some cases, defects were intentionally introduced into the single crystal methane hydrates by increasing the applied temperature driving force to 5 K at 14 MPa, which resulted in a third, semi-transparent hydrate morphology. The Raman Imaging results showed that the polycrystalline hydrates exhibited a much faster CH₄-CO₂ exchange rate compared to the single crystal hydrates. This arose due to the significant void space between the individual crystallines and the larger internal surface area for gas-solid mass transfer; defects and crystal imperfections may also have some effects on this rate as well. CO₂ molecules penetrated readily into the inner part of such particles, with CO₂ hydrate being present across 55% of the polycrystalline cross-section within 72 hours, and across 95 % of this cross-section in 120 hours. In contrast, the single crystal methane hydrates showed an extended stability during the exchange, with CO₂ hydrates being present across less than 1 % of the single crystal cross-section after 120 hours. Consequently, the shape of the single crystal methane hydrates remained intact with only a slight decrease in transparency. Results from single point measurements of semi-transparent hydrates show that the relative occupancy of CH₄ in the large and small hydrate cavities decreased as CO₂ replaced CH₄. Relative CH₄ occupancy was determined from the enclathrated ν_1 symmetric stretching peaks at 2906 cm⁻¹ and 2917 cm⁻¹ and the occupancy ratio changed from 3.12 (before exchange) to 1.15 (after exchange). While the relative CO₂ cage occupancy cannot be resolved from Raman spectra, the intensity of the enclathrated CO₂ signal increased as the CH₄ relative occupancy decreased, suggesting that the CO₂ molecules preferentially occupied the large 5¹²6² hydrate cages. The Raman images and spot measurements both suggested that a

diffusion-controlled guest molecule substitution process was taking place. The penetration depth of CO₂ into the semi-transparent methane hydrate (diameter $\approx 300\ \mu\text{m}$)—during a 5 day experiment—was around $50\ \mu\text{m}$ (ca. 33% radial penetration), which is consistent with the estimate of the diffusion coefficient ($8 \times 10^{-16}\ \text{m}^2\cdot\text{s}^{-1}$) from a Fick's Law analysis of the evolving CO₂ concentration profiles obtained from the fixed point Raman measurements. The diffusion rate of CO₂ through the transparent single crystal hydrate was extremely small, giving only small degrees of exchange in 5 days. Only a trace amount of CO₂ hydrates were detected by the Raman images after a 5 day exchange experiment with the transparent single crystal and the exchange process was restricted to the near-surface regions of the crystal. Overall, the morphology of methane hydrates, therefore, plays a critical role in the exchange process, which helps to explain the wide discrepancy of exchange rates for similar conditions reported in the literature. The results suggest that the rate is determined by both the rate of diffusion of the guest gas molecules within the hydrate matrix and the availability of sufficient local free volume for the hydrate water cages to re-arrange to enable CO₂ molecules to enter and replace the original CH₄ molecules. Both these processes would be expected to decrease in rate in the order polycrystalline > semitransparent imperfect crystals > transparent single crystals.

7.2 Contribution of This Work

This work has provided new insight and data for the formation rate of methane hydrates, their phase behaviour under confinement and rates of gas exchange as a function of hydrate physical state under pressure and temperature conditions relevant to natural gas hydrate systems and their potential exploitation. The research represents a significant step forward in our fundamental understanding of the way gas hydrates are formed and can be transformed. The collected data and derived parameters offer valuable inputs to process simulators concerning field exploration/production, and for potential uses in gas transportation and separation. These main outputs from this research are as follows:

- I. The design, fabrication and testing of a unique optical cell for Raman spectroscopy and imaging studies of multiphase systems. Such a cell, capable of fitting into the optical systems of a Raman microscope, is not available commercially and can be used to study not only gas hydrates but also a wide range of materials which require controlled confinement or are only stable/metastable well away from ambient conditions.
- II. The measurements of initial formation kinetics of methane hydrates, showing the dependency on hydrodynamic conditions, chemical potential differences, and the physical form and phases of the water precursor. Such measurements provide a benchmark for further kinetic studies. The data are consistent with a model comprising an intrinsic hydrate formation rate, the accessible gas-water interfacial area and a hydrate gas diffusion rate. The current work provides values for these rates which may be used in models of alternative gas hydrate formation processes.
- III. The production of a large set of experimental phase equilibrium data of confined methane hydrates over a wide range of temperature, pressure and pore sizes, in addition to the establishment of a correlation between the confined phase equilibrium and a modified Gibbs-Thomson equation.
- IV. The evaluation of the effect of pore surface chemistry on the confined melting points of methane hydrates. These effects have major implications for the stability and exploitation of gas hydrates in sediments of different mineralogies and wetting characteristics (Sandstone sediments tend to be water-wet whereas carbonate minerals tend towards mixed or oil-wet (hydrophobic) behaviour.).
- V. The demonstration for the first time of practical methods to control the hydrate morphology, from polycrystalline to essentially perfect single crystals, by manipulating the thermal driving force during hydrate.
- VI. The proof of how the initial morphology of the hydrate crystal affects the degree of $\text{CH}_4\text{-CO}_2$ exchange, which helps to explain the discrepancy of exchange rates for similar conditions reported in the literature.

7.3 Recommendation for Future Work

7.3.1 Further Experimental Investigations

A. Confined Phase Behaviour of Gas Hydrates

In this work, the phase behaviour of methane hydrates in porous media was studied. Such investigations should be extended to the phase behaviour of CO₂ hydrates and sII hydrates (i.e., methane and propane mixed gas), which would have major implications for the production and the CH₄-CO₂ exchange process of naturally occurring methane hydrate reservoirs.

An interesting direction of the porous media studies is the formation and phase equilibrium of confined gas hydrates from saline aquifers. It is commonly accepted that salt solutions inhibit the melting points of gas hydrates, similar to the confinement effect. However, salting-out and re-dissolution might have a greater impact on the phase behaviour of gas hydrates in confined media.

The confined melting points were measured solely using a High-Pressure DSC apparatus. An alternative technique would be helpful to confirm the findings. Powder XRD, NMR and MRI are practical options for equilibrium measurements of confined melting points, which demand customised high-pressure cells (shown in Figure 7.1).



Figure 7.1 High-pressure NMR tubing with copper fitting connected by epoxy resin “Figure courtesy of Crytur”

A few companies supply high-pressure NMR tubes, most of which are made from sapphire. Depending on the pressure rating required, the sapphire tube can be mounted on the copper/PEEK high-pressure connectors by epoxy or glass to metal soldering (i.e., silver nickel cobalt alloys).

B. Fabrication and Functionalisation of Porous Silica

The aqueous reaction used for modifying the surface chemistry of porous silica in this work posed a diffusion limitation in the liquid phase, resulting in partially reacted pore walls. In order to deal with this drawback, a vapour reaction at high temperatures might yield higher conversion rates and a uniform coverage ratio of the porous media. The silica-based porous media could be pre-treated by a plasma oxidation process, leading to a full coverage of hydroxyl groups on the surfaces. The resulting material and other precursors with functional groups could be further reacted in a flow reactor with nitrogen as a carrier gas. The temperature, the flow rate of the carrier gas and the amount of the reactants should also be carefully monitored and controlled.

Quantitative analysis of the surface chemistry inside porous materials is relatively complicated. A total organic carbon analysis might suggest some traces on the carbon coverage ratio inside the porous network. Meanwhile, a backscattered SEM would also give some quantitative information within a few microns from the surface. The preliminary results by the author also suggest that Temperature Programmed Reaction Spectroscopy (TPRS) would be suitable for quantitative analysis of the surface functional groups, which are burned off in an air environment at programmed high temperatures and the effluent gas analysed by an online mass spectroscopy.

Quantifying the surface tension could be considered as an alternative indicator to measuring the chemical composition of the pore wall. A force tensiometer utilising the capillary penetration method (also known as the Washburn method [207]) can be used to quantitatively investigate the surface energy of the fabricated silica material. In such tests, different fluids with known densities and viscosities are used to determine the contact angles. Based on trial

experiments by the author, the size of the powders (functionalised silica) and the packing density are crucial for the reproducibility of the experiment, suggesting that a consistent packing method should be employed.

C. Pore Size Measurements

Work of this sort requires accurate measurement of the pore size distribution of the host media. In this research a sensitive DSC apparatus could accurately determine the melting points of materials in confined media with a known pore size distributions. Similarly, when the melting properties of the fluid are known, DSC could also be used to quantitatively determine pore size distributions of an unknown material, which is known as thermoporometry [208]. It would be interesting to explore a fluid whose boiling point, or melting point is sensitive to the confinement effect. A comparison with other pore size measuring techniques is worth investigating, including NMR Cryoporometry [130], nitrogen BET measurements, and Mercury Intrusion Porosimetry (MIP).

D. Hydrate storage

In this work, it has been shown that the formation rate of methane hydrates was elevated in porous media, owing to the large contact areas generated by the porous structure. Gas hydrates have also been considered as gas storage media in many studies [209]. The main challenge is how to increase the formation rate and storage capacity of gas hydrates.

Silica-based aerogel, with porosity of 80%-99.8% [210], could be a suitable candidate for gas storage via the hydrate formation route. Metal organic frameworks (MOFs) have also demonstrated the storage potential of methane gas on its own [211]. It would be worth testing whether the gas storage capacity of these two types of media could be improved by the formation of gas hydrates.

It is also promising to combine a storage medium, like aerogel, MOFs and Dry Water, with hydrate promoters [Tetrahydrofuran (THF) or tetrabutylammonium bromide (TBAB)] which reduce the formation pressures of gas hydrates. Literature has shown that both THF and

TBAB destabilise Dry Water structures [110]. However, a different silica precursor for Dry Water might possibly stabilise a new Dry Water emulsion. Both Evonik and Wacker Chemie AG supply a range of silica precursors with variations in carbon contents and functional groups that can be investigated.

Formation kinetics within these storage media are generally measured by changes in pressures during the formation stage [110, 112, 114]. High-pressure thermogravimetric analysis is also suitable for hydrate formation kinetic studies.

E. Raman Measurements

The most time-consuming stage of the Raman study was the design and commissioning of the high-pressure cell. Therefore, it is worth extending the measurements to render more data from the Raman apparatus. Generally, the Stokes Raman signal is collected for most Raman measurements. With a suitable notch filter, it is possible to obtain anti-stokes Raman signals, which is temperature dependent. Such a temperature dependency has been applied to many applications including distributed temperature sensors [212] and measurements of the thermal conductivity [213]. The non-destructive and non-contact features of Raman-based temperature measurements could be extended to measure the thermal conductivity of materials under high pressures and to detect local reaction heat changes. Another interesting area is the temperature dependency of the Raman intensity. The dependency has been used to measure the hydrogen bond energy of water [214-217], which could be possibly extended to determination of hydrogen bond energy of gas hydrates under high pressures. The hydrogen bond energy of gas hydrates provides a nice link between the spectroscopy measurements and the bulk thermal properties (enthalpy) of hydrates. Surface Enhanced Raman Spectroscopy (SERS) on gas hydrates can be investigated by silver colloids. When water, contained in the silver colloids, are converted into gas hydrates, uniformly dispersed silver nanoparticles are expected to enhance the Raman intensity of the surrounding media (gas hydrates) by the Surface Enhanced Raman Effect.

The hydrate exchange study could be extended to other temperatures and pressures to consolidate the findings listed in this work. In real production processes via the CH₄-CO₂ exchange route, concentrations of methane are expected to increase over time, resulting in a mixture of methane and carbon dioxide in the reservoir and a reduction of the exchange rate. Exchange experiments with CH₄/CO₂ mixtures would shed light on such processes. Gas mixtures of N₂ and CO₂ were reported to enhance the recovery ratio of methane hydrates during the hydrate exchange process. It is possible that the gas mixture destabilises the hydrate structure and new mixed hydrates are formed either within the same hydrate crystal or somewhere else in the system. Such exchange experiments with a nearly perfect methane hydrate crystal could be investigated. A polarised Raman system would also be helpful to confirm the appearance of the crystal hydrates. A better understanding of the entire exchange process would be possible when considerable amounts of data, concerning variations in temperature, pressure, gas composition, and hydrate morphologies, have been accumulated.

As shown in Chapter 5, ¹³CO₂ and ¹²CO₂ have different Raman frequencies, suggesting that such phenomena can be applied to study diffusion related processes. For example, fully converted ¹²CO₂ hydrate can be synthesised, following by changing the surrounding gas to ¹³CO₂. Self-diffusion and exchange of CO₂ molecules can be tracked from the Raman spectra. Similarly, during CH₄-CO₂ experiments, different isotopes of CO₂ can be utilised at various stages to trace the source molecules of CO₂ hydrates.

7.3.2 Further Apparatus Improvements

A. High-pressure DSC Apparatus

Currently, the High-pressure DSC is not suitable for isochoric experiments since significant dead volumes exist in the pressure sensor's connector and the high-pressure valve. Implementation of a micro-valve and a flush diagram pressure sensor (Keller UK, 33X) should be considered to reduce the dead volume for isochoric experiments. The volume of the DSC high-pressure reactor (0.5 ml) curtails the options from most commercial high-pressure valves. Miniature high-pressure valves from Lee Products Ltd. could be used (see Figure 7.2).

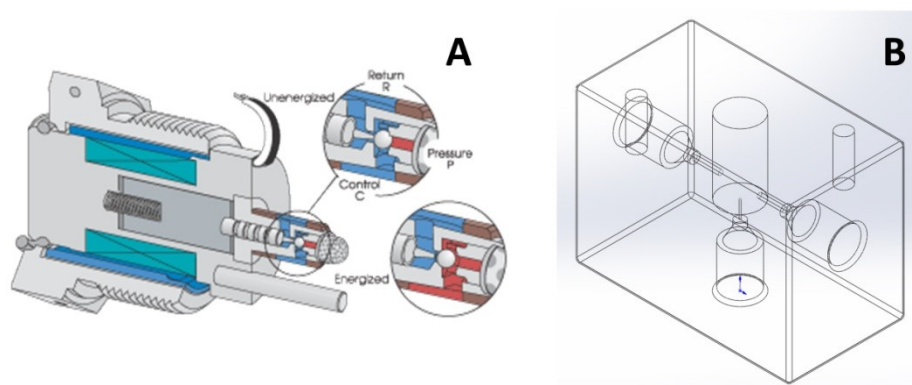


Figure 7.2 Customised high-pressure valve. A, Lee high-pressure valve; B, Valve manifold

With a closely machined manifold, the dead volume can be reduced to less than 20 μL . HIP or Sitec 1/16" fittings could be adopted for the high-pressure tubing connections. A similar manifold can also be made for a flush diagram pressure sensor (i.e., Keller UK Ltd) to further reduce the dead volume in the system.

B. Autoclave Reactor

The largest variation in the measurements made using the autoclave reactor stems from the pressure control and pressure measurements. As all components of the apparatus are remotely controlled except for the pressure regulation valve, an electronic high-pressure flow/pressure controller would allow full automation of the system and improve the accuracy of the measurements. A differential pressure sensor could be utilised when highly accurate pressure measurements are required. A high-pressure sampling valve (i.e., a Rolsi valve) and a gas chromatograph could be coupled to the system for mixed gas hydrate formation studies.

The garter seals used in the high-pressure reactor always failed to seal the pressure after approximately five to ten openings. A different garter seal material or an alternative sealing method should be explored. Potentially, an O-ring seal with a PEEK/PTFE backing gasket that is machined closely to the size of the original garter seal could be used.

Currently, a carbon filled PEEK bearing is used in the magnetically coupled stirrer. A relative small clearance (less than 0.2 mm) is provided to maintain the rotating magnet alignment, leading to friction losses and some resistances during operations. The bearing can be

improved by magnetic suspended bearings, which eliminate the contact surfaces of conventional bearings. The implementation of magnetic suspended bearings may lead to a smooth torque/current reading from the driving motors. Such modifications could potentially lead to a correlation between the output current of the driving motor and the viscosity of the fluid, enabling viscosity changes to be directly monitored during the hydrate growth process.

C. Raman High-pressure Reactor

The high-pressure optical reactor was designed to work statically and made from ferromagnetic steel due to its high mechanical strength. If a stirred system is of interest, a non-ferromagnetic material should be considered (i.e., 316 stainless steel). The stirrer could be driven by a few electromagnetic coils around the reactor, and the speed regulated by a suitable brushless DC motor controller.

High-pressure stainless steel tubing was found to be inconvenient to be used with moving stages, suggesting that flexible high-pressure PEEK tubing might be a suitable alternative. Vibrations from the circulated cooling path were able to propagate to the microscope moving stage, resulting in undesirable movements during the measurements. Such vibrations could be mitigated by using a buffer container which is firmly clamped. The Peltier controller is a PWM controller, outputting relative noisy power signals. Alternatively, a direct drive Peltier controller has higher efficiencies and a smooth power output. More precise temperature control inside the Raman enclosure could be considered, which could potentially upgrade the reactor to a calorimeter. A second Peltier-based condenser was also included in the Raman enclosure to eliminate condensation onto the optical window. Therefore, a dual output Peltier controller should also be given due consideration.

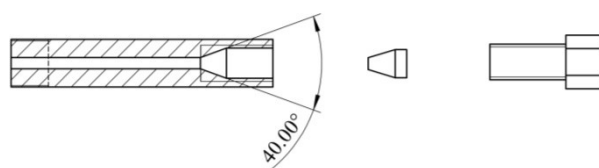


Figure 7.3 Valco (Cheminert) high-pressure fittings. Left, 1/4" adapter; Middle, 1/16" ferrule; Right, 1/16" nut.

Instead of having high-pressure female ports on the reactor directly, the reactor utilised four VICI 1/4" adapters in the current design, which is mainly due to the difficulties in duplicating the 40° angle (shown in Figure 7.3) in such a confined space. The 40° angled surface, on which the pressure seal occurs, has to be carefully polished with a special milling tool. It is worth obtaining the tools to eliminate the usage of 1/4" VICI adapters and so reducing the overall size of the reactor.

A blank top lid would be beneficial for detecting leakages on the pressure sealing ports. An anti-refractive sapphire window would also be helpful to enhance the intensity of weakly scattered Raman signals. The micro-valve and the flush diagram pressure sensor mentioned above in section 7.3.2A would also be applicable for the Raman reactor, concerning the small internal volume of the reactor (c.a. 0.7 ml). The performance of the aerogel-based insulation coating met the requirements, but increasing the thickness of the insulation layer would be beneficial. Another hydrophobic coating on top of the insulation would be helpful to minimise water absorptions on the coating surfaces at low temperatures. A slight modification of the top lid would allow *in-situ* XRD measurements to be made with hydrate crystals.

D. New Nucleation Kinetics Apparatus

Another interesting direction for gas hydrate research is better understanding of the nucleation phase of gas hydrate formation. It has been shown that the nucleation time of gas hydrates occurs with a probability distribution and is mainly controlled by temperature, pressure, and types of guest molecules. Understanding the probability of nucleation requires a large amount of data, which a conventional gas hydrate reactor can hardly provide within a short period of

time. Micro-fluidic chips have the potential to provide significant quantities of nucleation data by generating dozens of independent droplets in a single experiment [218, 219]. However, the application of microfluidic chips on gas hydrate research, especially high-pressure nucleation studies, has been limited.

The high-pressure chip could be obtained from Micronit but is limited to 10 MPa. With a suitable transparent bonding polymer (i.e., a thiolene-based optical adhesive), a high-pressure chip could be possibly made by bonding two sapphire or quartz plates via a lithography process [220]. High-quality images at low temperatures are crucial for the intended experiments, which might be potentially interrupted by condensations and vibrations at the experimental conditions. The high-pressure chip could be immersed in an aluminium container filled with fluids suitable for low-temperature applications (i.e., water-ethylene glycol mixtures). The aluminium container would be cooled by an external cooling jacket with circulated coolants. Precise temperature control could be realised by wire wound transparent heaters (i.e., from Northeast Flex Heaters Inc.) attached to the bottom of the high-pressure chip. It would also be advantageous to fuse temperature sensors (i.e., PT 100 elements) into the high-pressure chip.

An inverted microscope with an immersible objective could be used for imaging purposes. Thermal imaging cameras would also be helpful to confirm the uniformity of temperatures. It is also worth pointing out that X-ray cameras have a much higher resolution compared to that of light cameras. If an X-ray camera is considered, the high-pressure chip could be also made from two X-ray compatible metal plates sealed by O-rings. The internal channel could be made by laser engraving on one of the plates. Alternatively, using a newly emerging technique called selective metal melting (SLM) it might be possible to generate 3D structures with internal micro-channels.

Using modifications of the existing equipment and new devices such as those above will enable the current studies to be extended and built upon.

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Appendices

Appendix A Experimental data of reaction kinetics measurements

A1 Experimental data for formation kinetics of methane hydrates in the stirred water system

Pressure (MPa)	Temperature (K)	Rate ($\mu\text{mol}/\text{min}$)	Chemical Potential $\Delta\mu$ (10^{22} J)
50	278.5	12.02 ± 1.19	4.36
70	278.5	80.79 ± 14.27	15.65
80	278.5	112.90 ± 13.84	19.98
90	278.5	145.57 ± 16.85	23.72
105	278.5	217.97 ± 4.44	28.49
70	280.5	28.15 ± 4.84	8.85
90	280.5	90.66 ± 7.62	17.02
105	280.5	133.36 ± 1.81	21.86
50	276.5	36.93 ± 13.05	11.16
70	276.5	128.34 ± 8.51	22.33
80	276.5	185.30 ± 3.56	26.60
90	276.5	264.02 ± 9.11	30.29
90	283.5	27.01 ± 6.12	6.64
105	283.5	44.84 ± 7.31	11.59

A2 Experimental data for formation kinetics of methane hydrates in the stirred water system con.

No.	Pressure (MPa)	Temperature (K)	Rate (mmol/min)	R ²	Measured Pressure (10^2 kPa)	Measured Temperature (K)
Exp 1	5.0	278.5	0.01370	0.995	50.02 ± 0.05	278.41 ± 0.02
Exp 2	5.0	278.5	0.01033	0.993	49.66 ± 0.05	278.42 ± 0.02
Exp 3	7.0	278.5	0.06257	0.991	69.79 ± 0.14	278.50 ± 0.02
Exp 4	7.0	278.5	0.11367	0.991	69.46 ± 0.03	278.46 ± 0.01
Exp 5	7.0	278.5	0.06613	0.972	68.63 ± 0.01	278.48 ± 0.01
Exp 6	9.0	278.5	0.13046	0.992	88.37 ± 0.44	278.50 ± 0.02
Exp 7	9.0	278.5	0.12814	0.968	91.45 ± 0.11	278.45 ± 0.01
Exp 8	9.0	278.5	0.17812	0.991	89.36 ± 0.14	278.43 ± 0.04
Exp 9	10.5	278.5	0.20845	0.994	105.61 ± 0.15	278.47 ± 0.05
Exp 10	10.5	278.5	0.21944	0.995	105.75 ± 0.17	278.53 ± 0.01
Exp 11	10.5	278.5	0.22602	0.991	106.06 ± 0.08	278.50 ± 0.05
Exp 12	8.0	278.5	0.09740	0.991	79.42 ± 0.29	278.47 ± 0.01
Exp 13	8.0	278.5	0.14485	0.997	79.98 ± 0.31	278.57 ± 0.02
Exp 14	8.0	278.5	0.09645	0.995	80.69 ± 0.25	278.53 ± 0.02
Exp 15	7.0	280.5	0.02184	0.987	69.99 ± 0.14	280.49 ± 0.01

A3 Experimental data for formation kinetics of methane hydrates in the stirred water system con.

No.	Pressure (MPa)	Temperature (K)	Rate (mmol/min)	R ²	Measured Pressure (10 ² kPa)	Measured Temperature (K)
Exp 16	7.0	280.5	0.02332	0.986	70.36 ± 0.07	280.49 ± 0.01
Exp 17	7.0	280.5	0.03929	0.960	69.46 ± 0.1	280.52 ± 0.01
Exp 18	9.0	280.5	0.08259	0.978	90.83 ± 0.06	280.50 ± 0.01
Exp 19	9.0	280.5	0.11057	0.991	90.24 ± 0.03	280.47 ± 0.02
Exp 20	9.0	280.5	0.07567	0.991	90.07 ± 0.07	280.52 ± 0.01
Exp 21	9.0	280.5	0.09382	0.991	89.92 ± 0.05	280.58 ± 0.02
Exp 22	10.5	280.5	0.13745	0.985	105.25 ± 0.13	280.51 ± 0.04
Exp 23	10.5	280.5	0.13055	0.989	104.30 ± 0.05	280.50 ± 0.01
Exp 24	10.5	280.5	0.13209	0.979	106.31 ± 0.12	280.49 ± 0.01
Exp 25	5.0	276.5	0.02254	0.997	50.26 ± 0.06	276.52 ± 0.04
Exp 26	5.0	276.5	0.06707	0.987	50.06 ± 0.20	276.50 ± 0.02
Exp 27	5.0	276.5	0.02119	0.990	49.65 ± 0.07	276.47 ± 0.01
Exp 28	7.0	276.5	0.11202	0.985	70.09 ± 0.20	276.44 ± 0.04
Exp 29	7.0	276.5	0.14597	0.994	69.73 ± 0.06	276.49 ± 0.02
Exp 30	7.0	276.5	0.12703	0.993	70.53 ± 0.11	276.54 ± 0.01
Exp 31	8.0	276.5	0.19034	0.993	79.80 ± 0.18	276.46 ± 0.02
Exp 32	8.0	276.5	0.18026	0.982	79.05 ± 0.06	276.48 ± 0.01
Exp 33	9.0	276.5	0.30000	0.990	90.12 ± 0.19	276.44 ± 0.04
Exp 34	9.0	276.5	0.26304	0.999	89.97 ± 0.03	276.37 ± 0.06
Exp 35	9.0	276.5	0.26798	0.985	90.12 ± 0.04	276.46 ± 0.03
Exp 36	9.0	276.5	0.26103	0.981	89.49 ± 0.07	276.45 ± 0.02
Exp 37	9.0	283.5	0.03332	0.981	89.73 ± 0.05	283.48 ± 0.01
Exp 38	9.0	283.5	0.02777	0.983	88.71 ± 0.10	283.53 ± 0.01
Exp 39	9.0	283.5	0.01860	0.983	89.56 ± 0.02	283.43 ± 0.01
Exp 40	9.0	283.5	0.01208	0.985	88.39 ± 0.18	283.53 ± 0.01
Exp 41	9.0	283.5	0.04330	0.965	88.35 ± 0.31	283.53 ± 0.02
Exp 42	10.5	283.5	0.04190	0.986	102.10 ± 0.06	283.43 ± 0.01
Exp 43	10.5	283.5	0.03376	0.977	104.92 ± 0.08	283.52 ± 0.03
Exp 44	10.5	283.5	0.04475	0.992	105.38 ± 0.26	283.52 ± 0.10
Exp 45	10.5	283.5	0.02599	0.997	101.99 ± 0.31	283.52 ± 0.01
Exp 46	10.5	283.5	0.04109	0.982	104.99 ± 0.14	283.53 ± 0.01
Exp 47	10.5	283.5	0.05582	0.960	103.20 ± 0.24	283.42 ± 0.03
Exp 48	10.5	283.5	0.07056	0.997	104.37 ± 0.13	283.50 ± 0.02

A4 Experimental data for formation kinetics of methane hydrates in the stirred water system con.

No.	Rotating speed (rpm)	Rate (mmol/min)	R ²	Measured Pressure (10 ² kPa)	Measured Temperature (K)
Rate 1	630	0.04733	0.978	67.55 ± 0.13	278.49 ± 0.03
Rate 2	755	0.05745	0.994	70.01 ± 0.24	278.49 ± 0.02
Rate 3	755	0.06395	0.996	68.96 ± 0.07	278.40 ± 0.03
Rate 4	755	0.0619	0.991	72.57 ± 0.15	278.57 ± 0.02
Rate 5	800	0.07855	0.970	69.37 ± 0.05	278.53 ± 0.03
Rate 6	800	0.078	0.992	69.07 ± 0.08	278.50 ± 0.01
Rate 7	850	0.08143	0.996	69.75 ± 0.07	278.50 ± 0.02
Rate 8	850	0.10125	0.993	70.37 ± 0.12	278.43 ± 0.04
Rate 9	900	0.12686	0.993	68.18 ± 0.05	278.49 ± 0.02
Rate 10	950	0.017019	0.996	69.88 ± 0.14	278.55 ± 0.01
Rate 11	1000	0.21175	0.993	69.12 ± 0.10	278.60 ± 0.06
Rate 12	1000	0.25125	0.985	68.22 ± 0.09	278.58 ± 0.04
Rate 13	1000	0.20002	0.998	70.06 ± 0.11	278.47 ± 0.02
Rate 14	1000	0.21073	0.997	69.44 ± 0.14	278.42 ± 0.05
Rate 15	1000	0.21537	0.997	69.43 ± 0.16	278.40 ± 0.03
Rate 16	1000	0.21082	0.999	70.08 ± 0.05	278.35 ± 0.02
Rate 17	1100	0.25462	0.998	68.25 ± 0.04	278.52 ± 0.02
Rate 18	1200	0.31237	0.995	68.97 ± 0.28	278.59 ± 0.07
Rate 19	1200	0.28816	0.997	68.53 ± 0.24	278.47 ± 0.04
Rate 20	1300	0.40261	0.991	68.66 ± 0.16	278.54 ± 0.01
Rate 21	1300	0.37798	0.998	69.77 ± 0.15	278.46 ± 0.03

A5 Experimental data for formation kinetics of methane hydrates in the ice system con.

No.	Pressure (MPa)	Temperature (K)	Rate (mmol/min)	R ²	Measured Pressure (10 ² kPa)	Measured Temperature (K)
ICE 1	6.0	268.15	0.02210	0.996	59.20 ± 0.09	267.99 ± 0.07
ICE 2	6.0	268.15	0.02845	0.992	59.81 ± 0.18	268.22 ± 0.02
ICE 3	6.0	268.15	0.02070	0.969	59.59 ± 0.03	268.11 ± 0.03
ICE 4	4.0	268.15	0.01332	0.982	40.55 ± 0.15	268.20 ± 0.01
ICE 5	4.0	268.15	0.01205	0.998	39.36 ± 0.31	268.30 ± 0.02
ICE 6	3.0	268.15	0.00716	0.989	31.93 ± 0.12	268.06 ± 0.02
ICE 7	3.0	268.15	0.00802	0.990	31.44 ± 0.10	268.12 ± 0.02

A6 Experimental data for formation kinetics of methane hydrates in the dry water system con.

No.	Pressure (MPa)	Temperature (K)	Rate (mmol/min)	R ²	Measured Pressure (10 ² kPa)	Measured Temperature (K)
DW 1	7.0	278.5	0.46733	0.996	68.21 ± 0.07	278.45 ± 0.30
DW 2	7.0	278.5	0.28206	0.994	67.89 ± 0.07	278.49 ± 0.28
DW 3	7.0	278.5	0.50303	0.997	68.24 ± 0.06	278.47 ± 0.05
DW 4	7.0	278.5	0.49597	0.996	68.12 ± 0.04	278.58 ± 0.04
DW 5	7.0	278.5	0.51862	0.996	67.59 ± 0.02	278.58 ± 0.08
DW 6	7.0	278.5	0.61949	0.965	67.55 ± 0.07	278.59 ± 0.21
DW 7	7.0	278.5	0.51060	0.987	68.92 ± 0.13	278.53 ± 0.16
DW 8	8.0	278.5	0.71191	0.993	78.19 ± 0.10	278.52 ± 0.01
DW 9	8.0	278.5	0.98445	0.997	78.63 ± 0.09	278.46 ± 0.20
DW 10	8.0	278.5	0.99140	0.998	77.31 ± 0.07	278.46 ± 0.04
DW 11	8.0	278.5	0.70512	0.993	78.96 ± 0.07	278.46 ± 0.06
DW 12	5.0	278.5	0.00455	0.987	51.14 ± 0.07	278.49 ± 0.02
DW 13	9.0	278.5	2.06185	0.995	89.58 ± 0.08	278.57 ± 0.08
DW 14	9.0	278.5	1.77923	0.995	88.36 ± 0.04	278.60 ± 0.08
DW 15	9.0	278.5	1.90013	0.995	88.51 ± 0.11	278.56 ± 0.06
DW 16	9.0	278.5	1.39146	0.991	90.62 ± 0.03	278.48 ± 0.02
DW 17	5.0	278.5	0.00543	0.987	47.79 ± 0.05	278.43 ± 0.02
DW 18	5.0	278.5	0.01018	0.989	52.05 ± 0.04	278.50 ± 0.03
DW 19	5.0	278.5	0.01607	0.988	50.37 ± 0.04	278.50 ± 0.03
DW 20	8.0	276.5	1.60161	0.984	79.72 ± 0.19	276.4 ± 0.33
DW 21	8.0	276.5	1.95097	0.994	79.09 ± 0.17	276.41 ± 0.28
DW 22	8.0	276.5	1.71117	0.996	77.95 ± 0.49	276.42 ± 0.18
DW 23	8.0	276.5	1.31498	0.982	76.73 ± 0.05	276.39 ± 0.22
DW 24	8.0	276.5	1.94254	0.998	79.31 ± 0.10	276.41 ± 0.28
DW 25	8.0	276.5	1.94684	0.997	79.82 ± 0.20	276.43 ± 0.23

Appendix B Experimental data of hydrate phase equilibrium measurements

A7 Experimental data for phase equilibrium of methane hydrates in porous silica

Pressure (MPa)	Pore size (nm)	Melting Point (K)	Pressure (MPa)	Pore size (nm)	Melting Point (K)
50	8.5	292.25±0.07	15	40.3	288.37 ± 0.02
40	8.5	290.51 ± 0.01	10	40.3	285.05 ± 0.02
30	8.5	288.46 ± 0.09	7.5	40.3	282.60 ± 0.06
20	8.5	285.54 ± 0.07	5	40.3	278.63 ± 0.03
15	8.5	283.43 ± 0.09	50	95.4	298.14 ± 0.01
10	8.5	280.32 ± 0.08	40	95.4	296.30 ± 0.03
7.5	8.5	277.83 ± 0.03	30	95.4	294.09 ± 0.01
5	8.5	274.10 ± 0.07	20	95.4	291.04 ± 0.01
50	17.1	295.73 ± 0.02	15	95.4	288.85 ± 0.01
40	17.1	293.90 ± 0.06	10	95.4	285.53 ± 0.01
30	17.1	291.67 ± 0.06	7.5	95.4	282.88 ± 0.06
20	17.1	288.59 ± 0.09	5	95.4	279.11 ± 0.03
15	17.1	286.53 ± 0.08	50	195.7	298.53 ± 0.02
10	17.1	283.30 ± 0.05	40	195.7	296.73 ± 0.01
7.5	17.1	280.67 ± 0.06	30	195.7	294.52 ± 0.02
5	17.1	276.92 ± 0.01	20	195.7	291.40 ± 0.01
50	34.8	297.20 ± 0.02	15	195.7	289.27 ± 0.01
40	34.8	295.43 ± 0.03	10	195.7	285.85 ± 0.01
30	34.8	293.25 ± 0.01	7.5	195.7	283.26 ± 0.08
20	34.8	290.28 ± 0.01	5	195.7	279.43 ± 0.03
15	34.8	288.01 ± 0.09	50	Bulk	298.62 ± 0.02
10	34.8	284.76 ± 0.02	40	Bulk	296.87 ± 0.05
7.5	34.8	282.18 ± 0.02	30	Bulk	294.68 ± 0.07
5	34.8	278.41 ± 0.04	20	Bulk	291.49 ± 0.04
50	40.3	297.68 ± 0.02	15	Bulk	289.45 ± 0.03
40	40.3	295.86 ± 0.01	10	Bulk	286.09 ± 0.07
30	40.3	293.62 ± 0.02	7.5	Bulk	283.42 ± 0.03
20	40.3	290.61 ± 0.04	5	Bulk	279.78 ± 0.05

Appendix C Pressure vessel design calculations

A8 Pressure vessel design calculations

Conditions		
Fluid State	1	Gas or (Gas + Liquid)
Fluid Group	1	Hazardous fluids
$p_w/\text{MPa} =$	50	Maximum working pressure
$T_w/^\circ\text{C} =$	80	Maximum working temperature
$p_{\text{test}}/\text{MPa} =$	75	Hydrostatic test pressure
Material:	17-4 PH steel	Martensitic precipitation-hardening 17-4 PH Condition A (AK Steel)
$\sigma_y/(\text{N}/\text{mm}^2) =$	1000	0.2% Yield stress at maximum service temperature
$\sigma_{\text{utmr}}/(\text{N}/\text{mm}^2) =$	1103	Ultimate tensile stress at maximum service temperature
$M =$	4	Shear stress safety factor
$\tau_{\text{max}}/(\text{N}/\text{mm}^2) =$	125	Maximum shear stress, including safety factor
Material:	Sapphire	
$\sigma_y/(\text{N}/\text{mm}^2) =$	280	Yield stress at maximum service temperature
$\sigma_u/(\text{N}/\text{mm}^2) =$	1900	Ultimate tensile stress at maximum service temperature
$M =$	4	Shear stress safety factor
S_f/MPa	448	Fracture Strength/Modulus to Rupture
$\tau_{\text{max}}/(\text{N}/\text{mm}^2) =$	35	Maximum shear stress, including safety factor
Material:	Bolt	
$\sigma_y/(\text{N}/\text{mm}^2) =$	311	0.2% Yield stress at maximum service temperature
Material:	VICI 1/4" Tubing	
$\sigma_y/(\text{N}/\text{mm}^2) =$	290	316 Stainless Steel 0.2% Yield stress at maximum service temperature
Cylinder		
ID/mm =	10.0	ID of cylinder
OD/mm =	43.0	OD of cylinder
L/mm =	6.0	Internal length
V/mL =	0.47	Max. internal volume
K =	4.3	Ratio between OD and ID of cylinder
$\frac{2}{3}p_y/\text{MPa} =$	315.3	Yield stress criterion: $p_w \leq \frac{2}{3}p_y$ $P_y = \frac{\sigma_y}{2} \cdot \left(\frac{K^2 - 1}{K^2} \right)$
$\frac{1}{4}p_u/\text{MPa} =$	343.4	Burst pressure criterion: $p_w \leq \frac{1}{4}p_u$, $P_u = 2\sigma_u \cdot \left(\frac{K - 1}{K + 1} \right)$

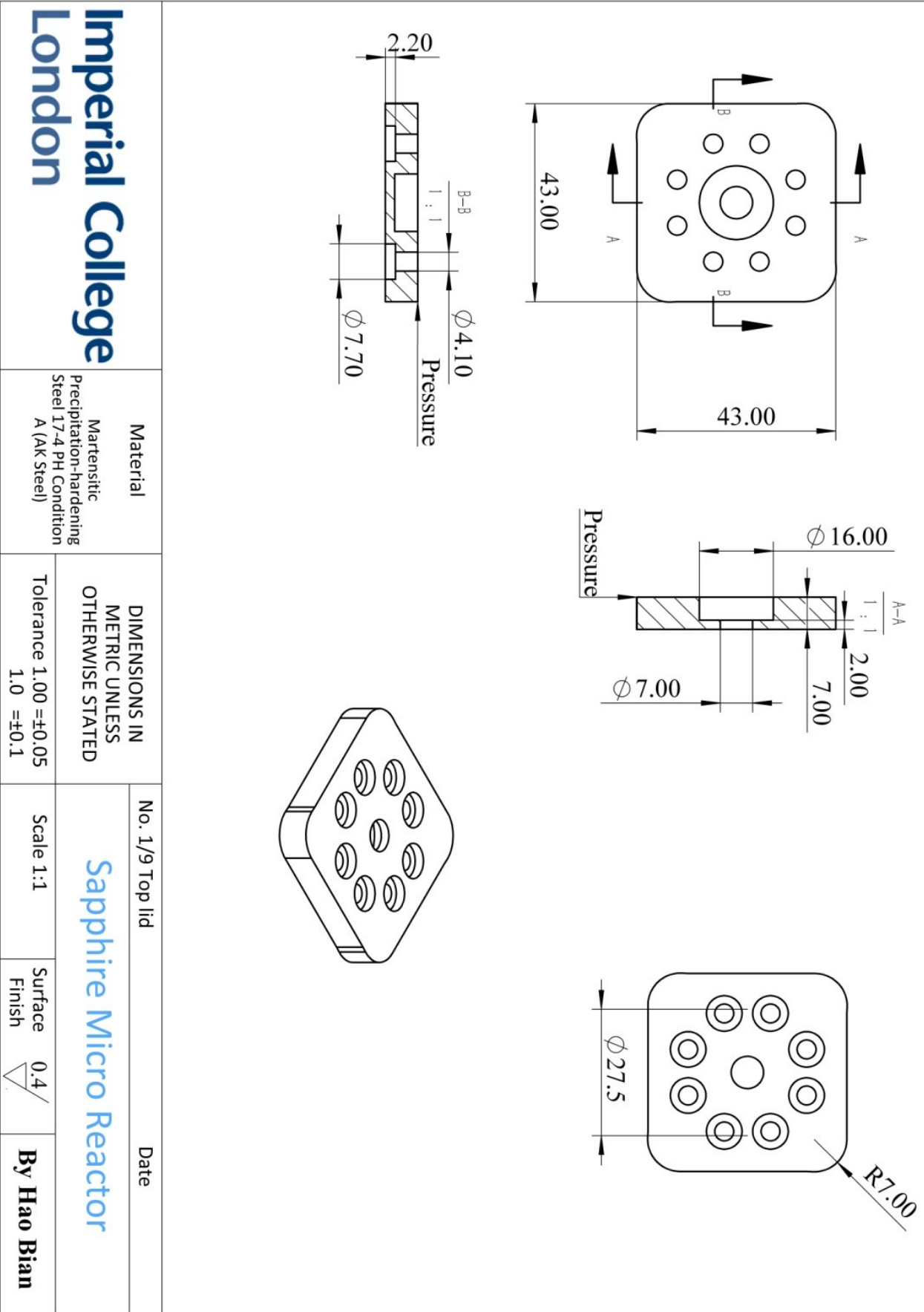
A9 Pressure vessel design calculations continued

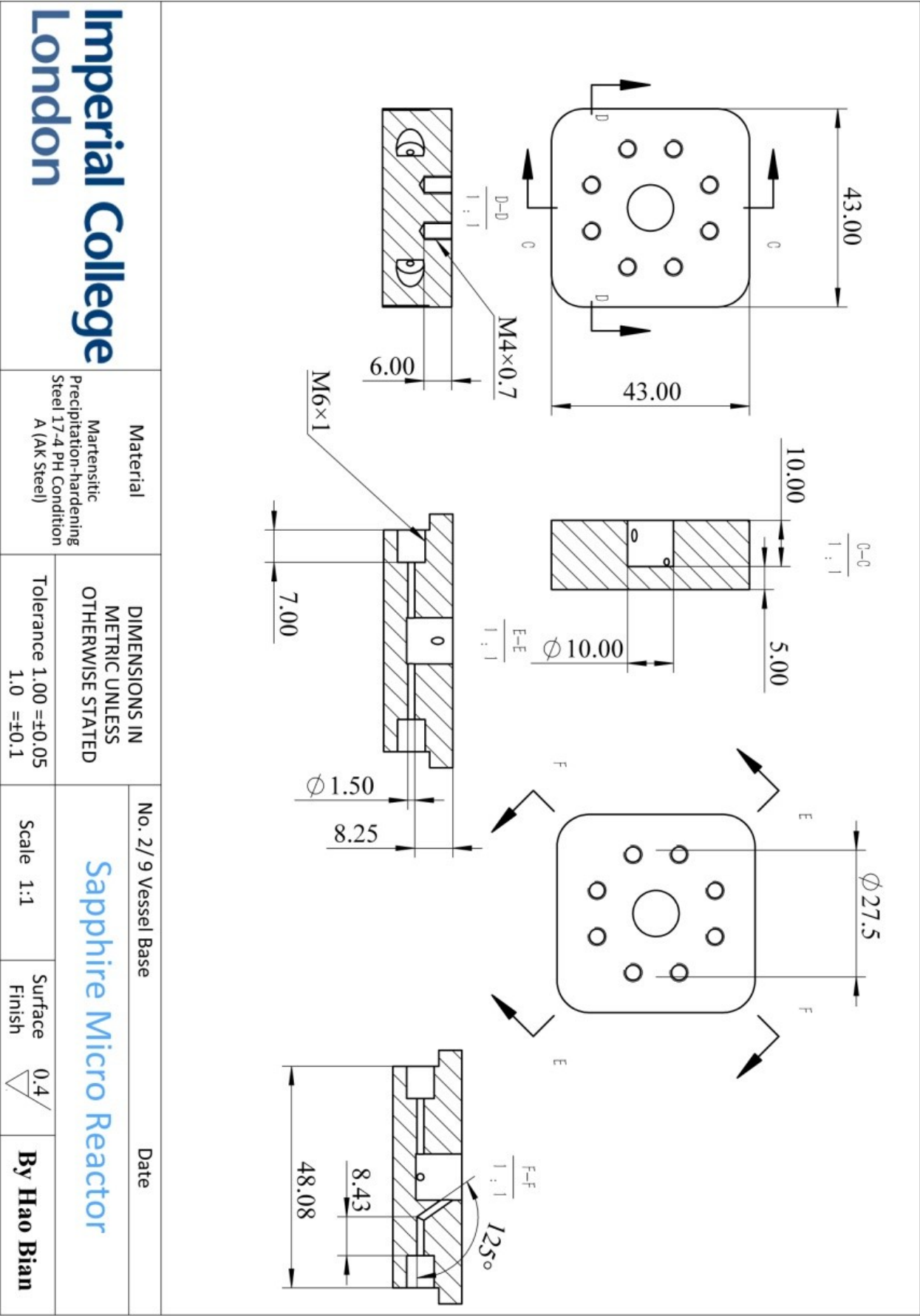
Base t/mm = (4t $\tau_{\max}$ /D)/MPa =	5.0	Thickness of base
	250.0	
Thickness of Sapphire Window Aw/mm Kw SF td/mm Pd/MPa tw/mm	10.0 1.25 4 6.0 50.0 3.7	Window Aperture in Diameter Support Condition Parameter (Unclamped 1.25, Clamped 0.75 Safety Factor Design thickness Pressure Difference Minimal Thickness
Top Plate h _{lid} thickness 1/mm = h _{lid} thickness 2/mm = D1/mm = D2/mm= (4D ₂ h ₂ $\tau_{\max}$ /D ²)/MPa = (4D _t L _t $\tau_{\max}$ /D ²)/MPa =	2 4.8 16 16 62.5 150.0	Lid thickness 1 Lid thickness 2 Effective sealing diameter Groove Diameter 1 Effective sealing diameter Groove Diameter 2 Lid shear stress criterion (Shear Stress Point 1) Lid shear stress criterion (Shear Stress Point 2)
Plate End Closure (Bolted) e/mm = N _b = A _b /mm ² G/mm = C/mm = p _d /MPa = S _{FO} /(N/mm ²) = H/N = H _G /N = e _{min} /mm = A _{bmi} /mm ² = N =	7 6 8.8 16 30 60 666.7 12064 1005.31 4.8 42.0 4.8	End closure thickness Number of bolts Tensile area of one bolt M4 Gasket sealing diameter Bolt circle diameter Flange design pressure Flange design stress Hydrostatic end load Gasket compression load PTFE 100% strain at 15 MPa Minimum end closure thickness (BS5500) Minimum bolt area Minimum number of bolts

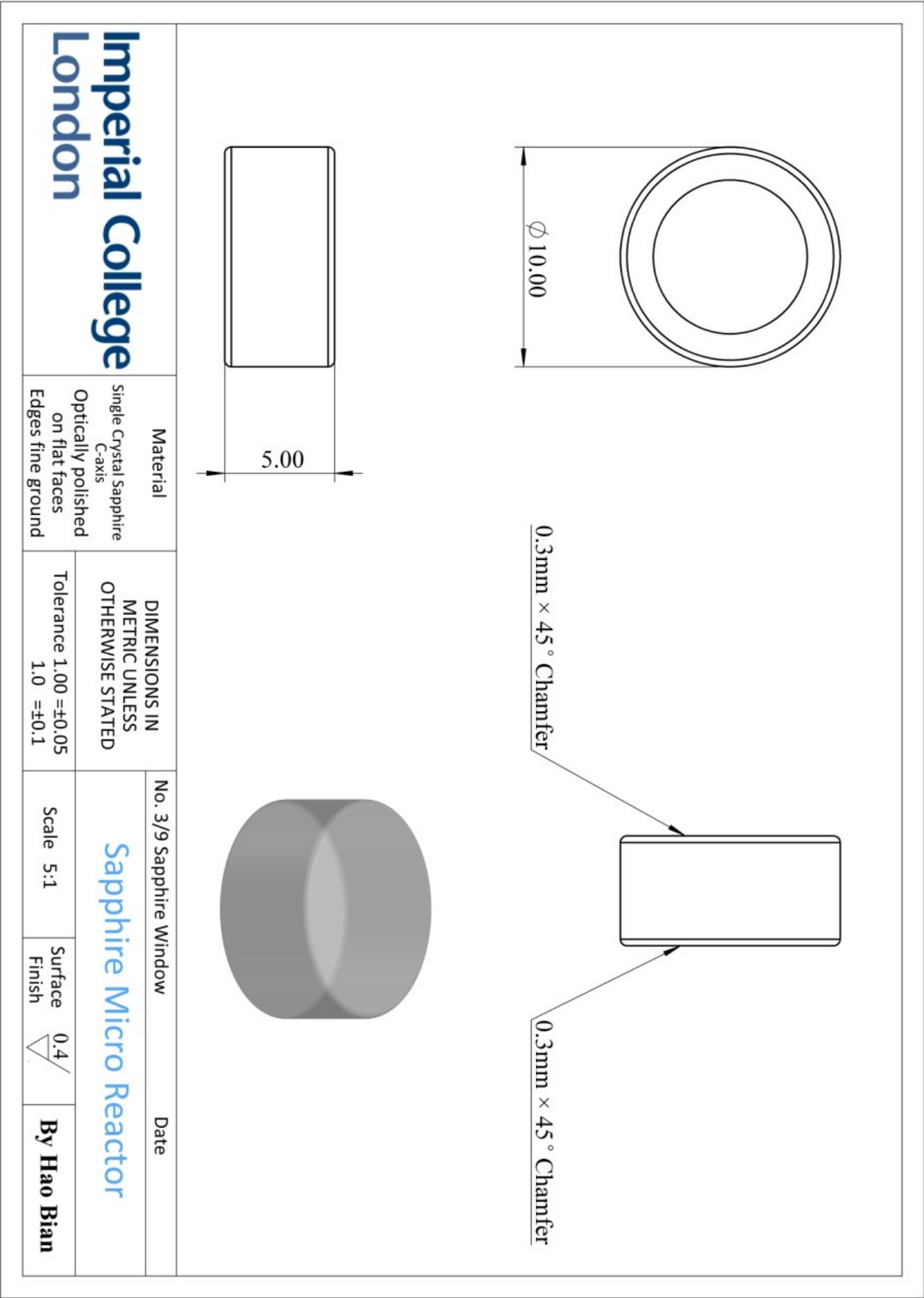
A10 Pressure vessel design calculations continued

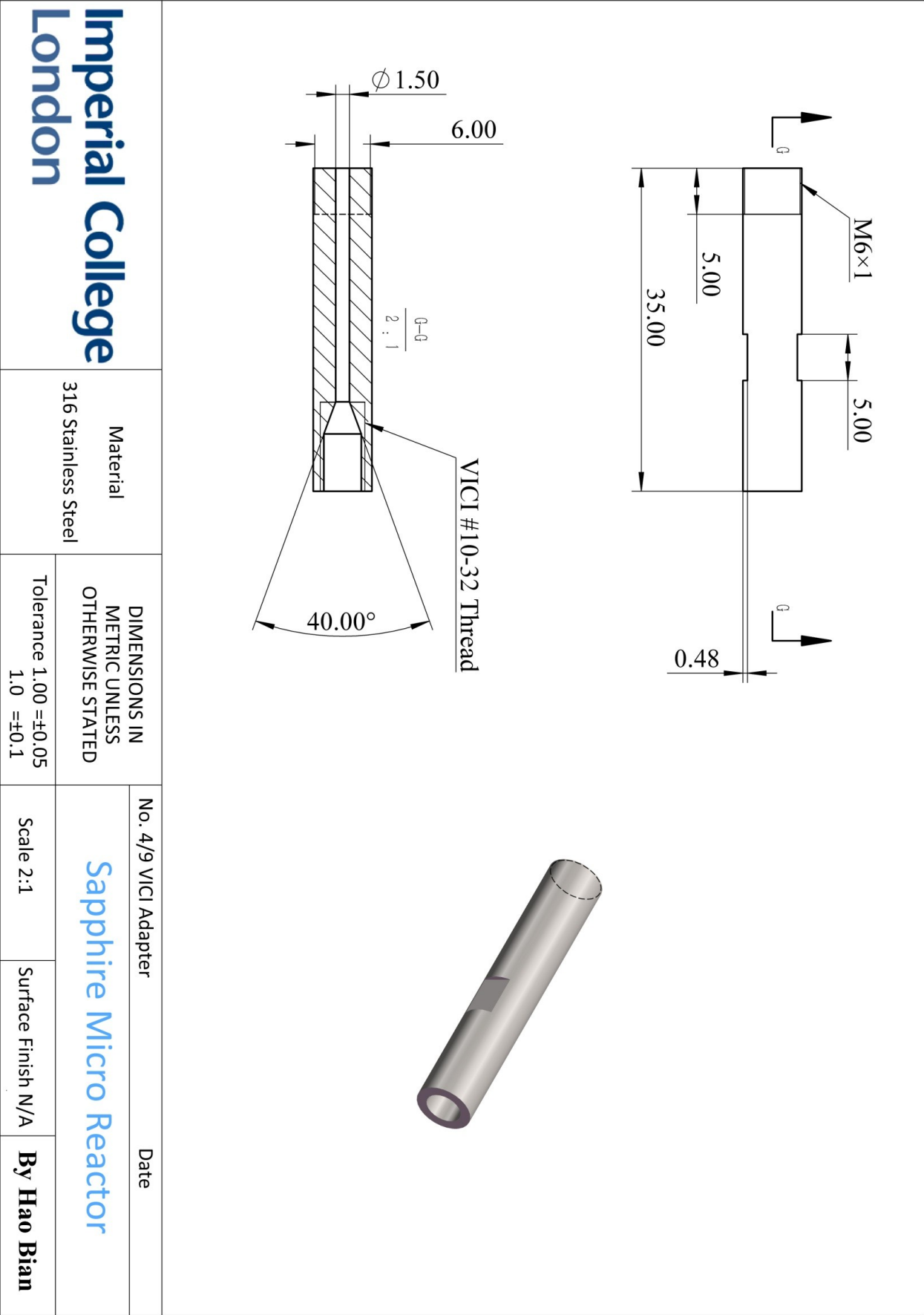
Plate Shear Stress		
D/mm =	16	Effective sealing diameter
h _l /mm =	4.8	Plate minimal thickness
n	6	Number of bolts
D _l /mm =	7.7	Hole Diameter
(4nD _l h _l τ _{max} /D ²)/MPa =	433.1	Plate shear stress criterion (Shear Stress Point A)
VICI 1/4" Thread Load		
A _b /mm ²	20.1	Tensile area of M6
G/mm =	6	Gasket sealing diameter
p _d /MPa =	60	Design pressure
S _{FO} /(N/mm ²) =	210.2	Design stress
H/N =	1696	Hydrostatic end load
H _G /N =	424.1	Gasket compression load PTFE 100% strain at 15 MPa
A _{bm} /mm ² =	7.3	Minimum Tensile area
VICI 1/4" Thread Length		
Type of Thread	M4	
p/mm=	0.7	Pitch
Dmax/mm=	3.2	Maximum minor diameter of internal thread
dmin/mm=	4.0	Minimum major diameter of external thread
Ass/mm2=	8.7	External thread shear area
St/N/mm2=	450	Material Tensile strength
P/N/mm2=	50	Loading pressure
A/mm2=	78.5	Area under Pressure
LE/mm=	2.5	Length of engagement
Type of Thread	M6	
p/mm=	1	Pitch
Dmax/mm=	4.9	Maximum minor diameter of internal thread
dmin/mm=	6.0	Minimum major diameter of external thread
Ass/mm2=	4.9	External thread shear area
St/N/mm2=	290	Material Tensile strength
P/N/mm2=	50	Loading pressure
A/mm2=	28.3	Area under Pressure
LE/mm=	1.4	Length of engagement

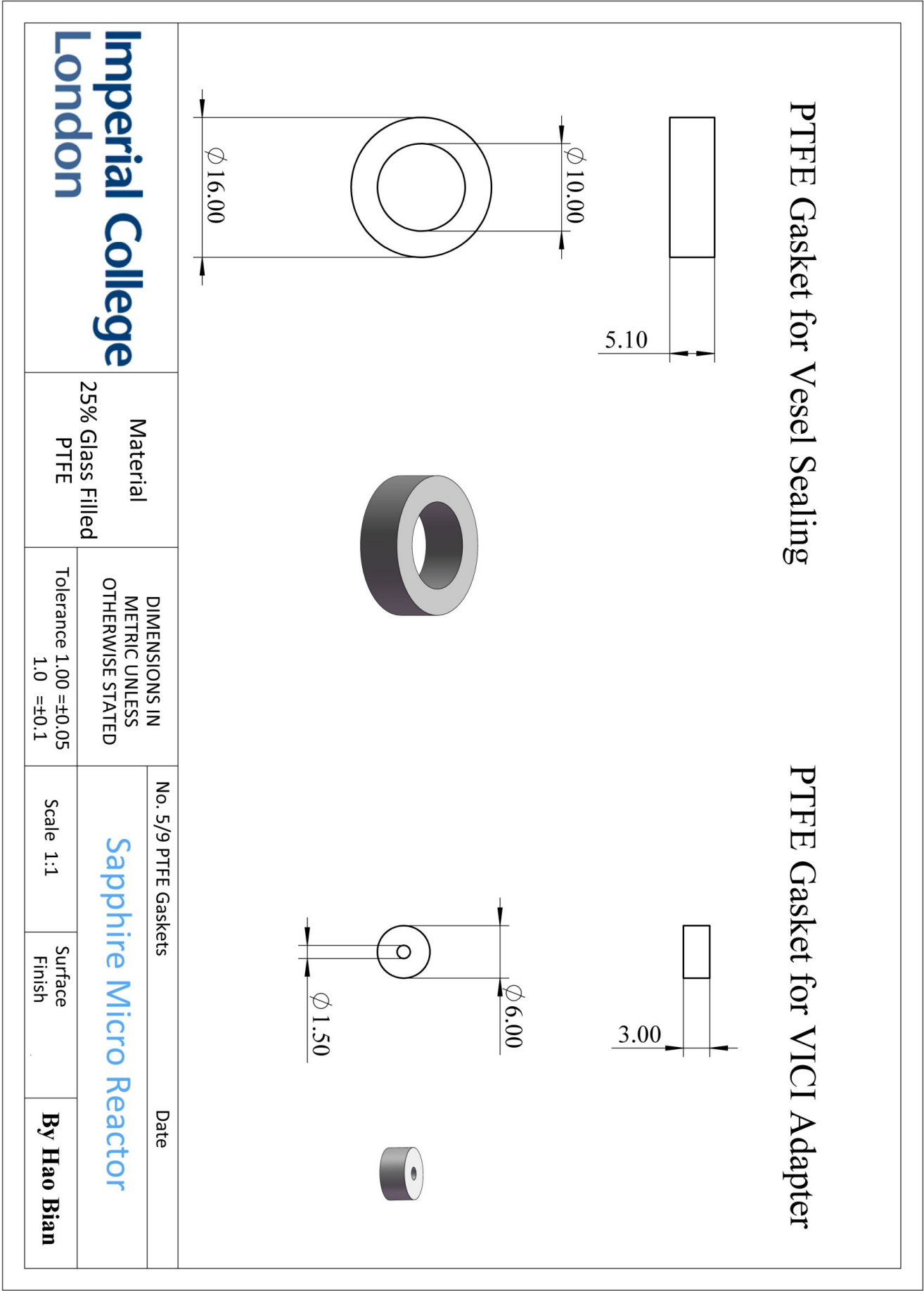
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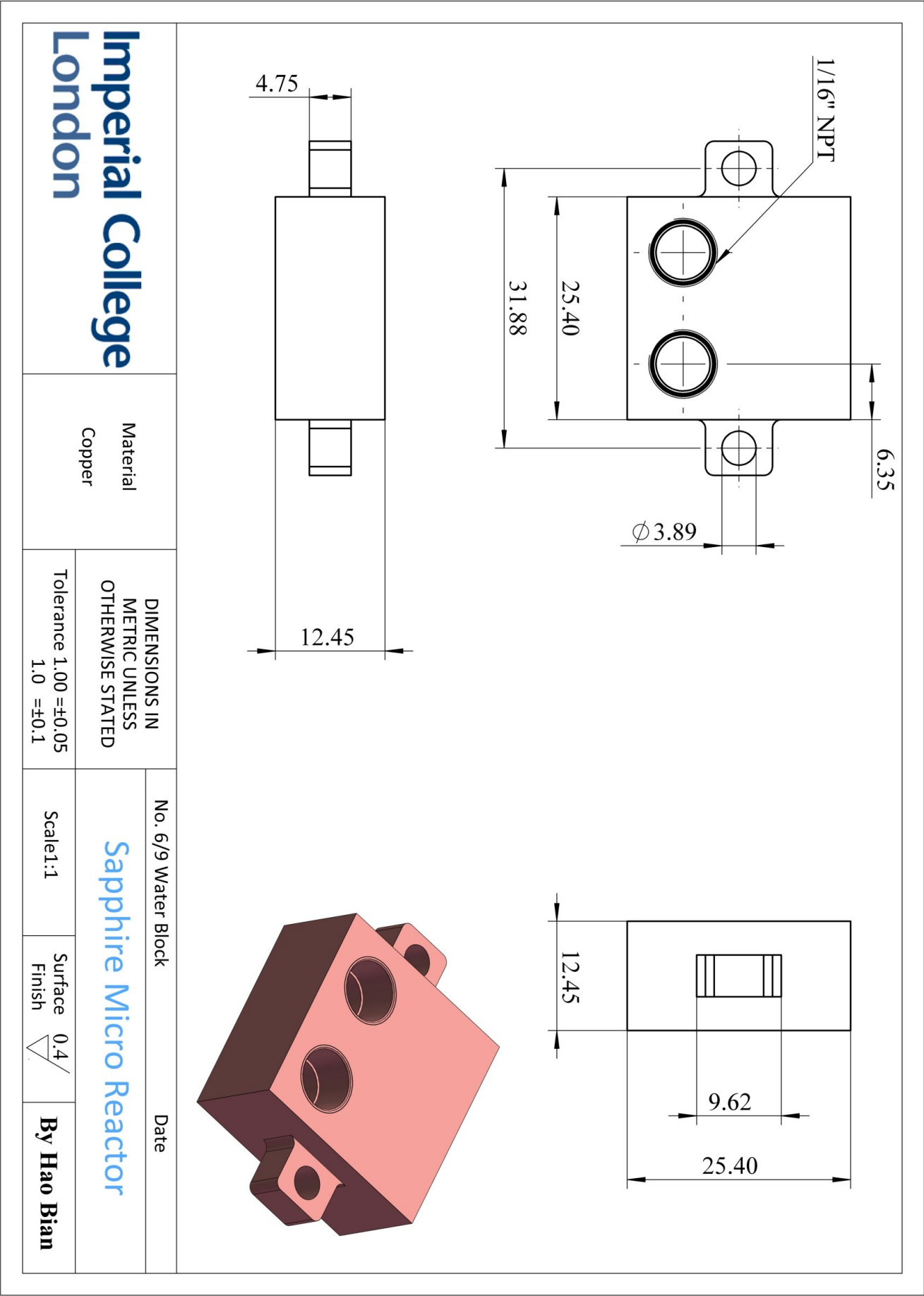


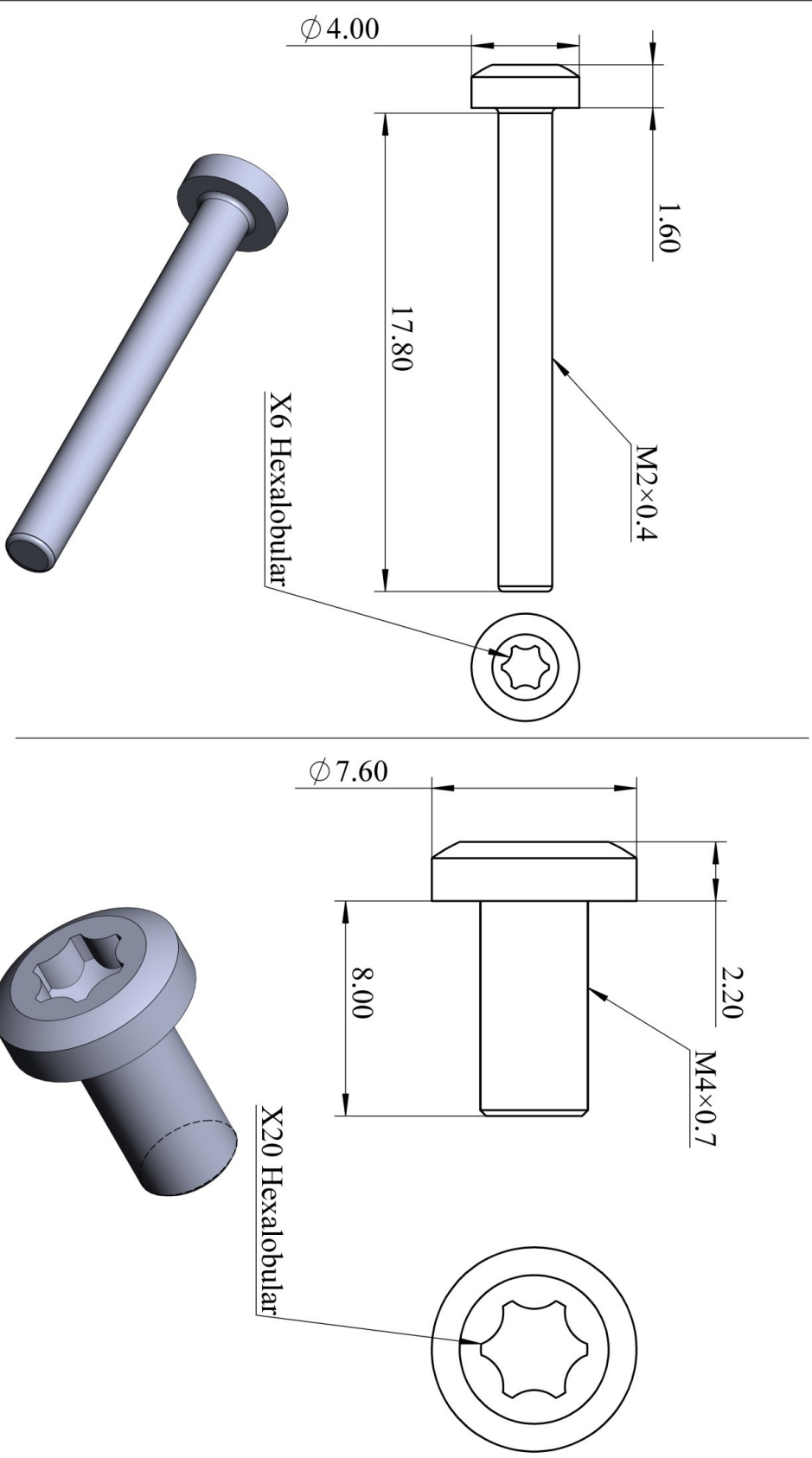






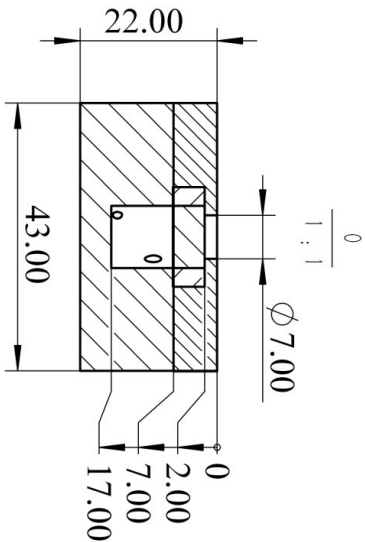
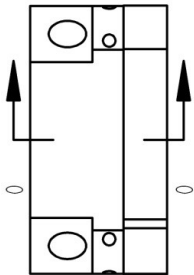
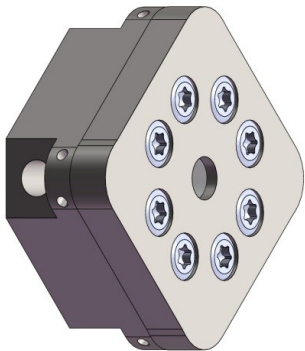


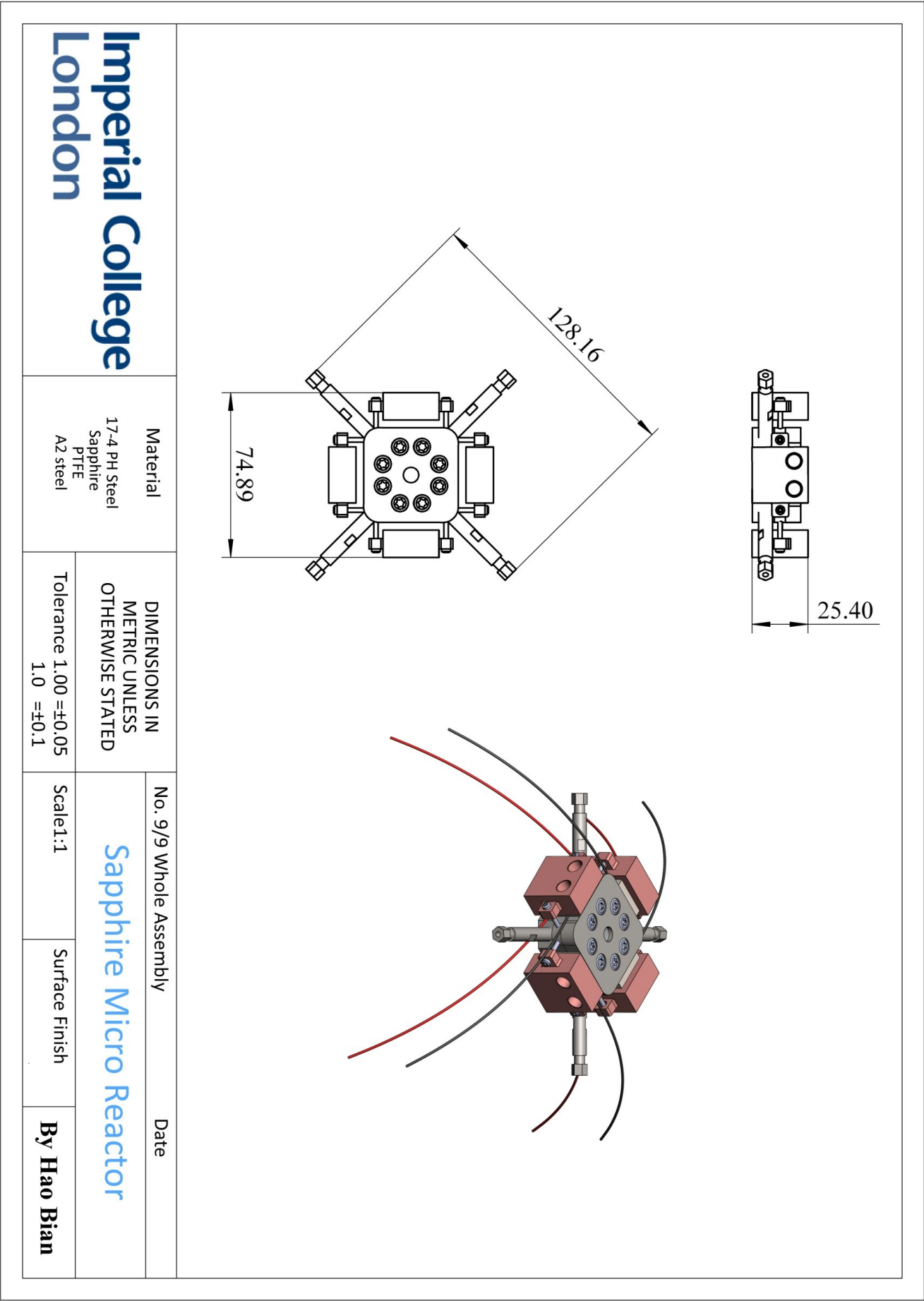




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				Tolerance 1.00 =±0.05 1.0 =±0.1		Scale 5:1		Surface Finish N/A	
						Sapphire Micro Reactor		By Hao Bian	

Imperial College London		Material 17-4 PH Steel Sapphire PTFE A2 steel		DIMENSIONS IN METRIC UNLESS OTHERWISE STATED		No. 8/9 Vessel Assembly		Date	
				Tolerance 1.00 =±0.05 1.0 =±0.1		Sapphire Micro Reactor			
						Scale 1:1		Surface Finish N/A	
								By Hao Bian	





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3	11	Figure 2.3 Field-emission scanning electron images of CH ₄ hydrates synthesised from ice.	Staykova et al. [31]	American Chemical Society	Written permission via CCC
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11	121	Figure 6.1 Schematic of Renishaw InVia Reflex Raman spectrometer.	Renishaw InVia Manual	Renishaw	Email

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No. 5 - Figure 2.6 Hydrate Stable Zones in Deep Sea Area of Methane Hydrate

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No. 9 - Figure 3.15B Dry water

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Publication: Journal of the American Chemical Society

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Date: Sep 1, 2008

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