KINETIC, EQUILIBRIUM AND MORPHOLOGY STUDIES OF HYDRATE FORMING SYSTEMS

By

PHILLIP SERVIO

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Approved by ______

Chairperson of Supervisory Committee

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Department of <u>Chemical & Bislogical Engineering</u>

The University of British Columbia Vancouver, Canada

Date Febrary 11/02

ABSTRACT

Gas hydrates are nonstoichiometric crystalline compounds that form naturally in certain environments on earth. Gas hydrates have been viewed as a nuisance in the oil and gas industry because they may impede oil and gas operations. On the other hand, hydrates are getting recognition as a potential future energy source. Furthermore, in situ methane hydrate is linked to global warming and carbon dioxide hydrate is linked to carbon dioxide sequestration. In this work, certain kinetic, equilibrium and morphological data were obtained. Such data is useful for the design of safe and economical technologies for gas transportation and storage and facilities to allow exploitation of gas hydrates. Specifically the following issues were addressed in this work.

Measurements of the solubility of methane and carbon dioxide gas in liquid water in the presence of gas hydrates have been obtained. It is known that in the absence of gas hydrates the solubility of methane and carbon dioxide increases with decreasing temperature. It was found that the presence of hydrates changes this trend such that the solubility of methane and carbon dioxide decreases with decreasing temperature. The data agree well with theoretically calculated values. This information removes a controversy that existed in the literature.

Equilibrium studies were performed on structure H hydrate forming system of methane-carbon dioxide-neohexane-water. It was found that the presence of neohexane greatly decreased the hydrate equilibrium pressure. It was also found that the composition of the gas phase affected the hydrate equilibrium conditions. The lowering of the equilibrium formation pressure favors the conditions for gas storage and transportation.

A laser light scattering technique was employed in order to establish a new method to extract kinetic data. Hydrate growth experiments were performed using ethane-water as a model system for convenience. These experiments where conducted in the presence of monodispersed latex spheres of known size and charge. The study was inconclusive in ascertaining if the presence of latex particles had any effect on the nucleation or growth of hydrate crystals.

Morphological studies on structure I hydrates (methane and carbon dioxide) where performed on water droplets under different driving forces for hydrate nucleation in order to elucidate the mechanistic aspects of hydrate nucleation, growth, and

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decomposition. The driving force was defined as the deviation of the experimental pressure from the equilibrium hydrate formation pressure at the experimental temperature. Studies showed that higher driving forces gave smaller nucleation times along with jagged sharp surfaces. Lower driving forces gave larger nucleation times with smoother surfaces.

Morphology studies were also performed on the structure H forming system of methane-neohexane-water. Observations concluded that the rate of growth of structure H hydrate crystals was much more rapid then those of structure I. The kinetics of growth were also found to depend on the amount of time methane was allowed to dissolve into neohexane and not the magnitude of the driving force present.

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Chapter 1

INTRODUCTION

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Hydrates are nonstoichiometric crystalline compounds belonging to the inclusion group known as clathrates. Hydrates occur when water molecules hydrogen bond and form cavities. These cavities may then be occupied by a gas or volatile liquid whose presence inside the lattice thermodynamically stabilizes the hydrate. There is no chemical reaction or chemical bonding between the host lattice and guest molecule, only physical bonding via weak van der Waals forces.

Sir Humphry Davy is credited with the discovery of hydrates in 1810 (Englezos, 1993; Sloan, 1998a; Makogon, 1997). He observed that chlorine gas in a solution of water could freeze at temperatures as high as 9.0°C. This observation was later confirmed by Faraday who suggested that the composition of the compound was approximately 1 part chlorine and 10 parts water. These findings were the start of hydrate research and it has since developed into a major area with many different specializations.

Since the discovery of hydrates in 1810 until early 1900, the research mainly concentrated around finding compounds that could form hydrates in the presence of water and determining the composition of gas hydrates. Hammerschmidt (1934) discovered that hydrates could also form and plug natural gas pipelines. With this discovery hydrates quickly gained industrial interest. The amount of research being done increased tremendously and started to focus on the prediction of hydrate formation and on ways of inhibiting hydrate formation.

Another step in hydrate research occurred in 1965 when the first discovery of in situ hydrates was made in the Siberian permafrost by Makogon and co-workers (Sloan, 1998a; Makogon, 1997). This lead to hydrate research being done in the field of recovering in situ gas hydrates. Hydrates were now viewed as a potential energy source of the future due to this discovery. Reason being that the composition of these naturally occurring hydrates in the earth was mostly methane, the main component of natural gas.

Naturally occurring methane hydrates in the earth and ocean could also be potentially dangerous to the global environment (Englezos, 1993; 2001; Sloan, 1998a; Makogon, 1997; Kvenvolden, 1993; 1999). If global warming occurs, the temperature will rise and hence decompose methane hydrates present in the earth. Methane is one of the most harmful greenhouse gases and this effect could be potentially threatening. On the other hand conversion of natural gas into hydrate and the transportation of natural gas in hydrate form posses an economical alternative to the transportation of liquefied or compressed natural gas (Kokhar et al.,1998; 2000). Thus, methane hydrate is important from both an environmental and an energy point of view.

Carbon dioxide hydrate is also an important hydrate for a number of reasons. Carbon dioxide, like methane, is also a component of natural gas and may form hydrates in oil reservoirs during enhanced oil recovery, thereby causing complications. Carbon dioxide is also a harmful greenhouse gas and is a major component in the emissions of thermal power plants. If carbon dioxide from thermal power plants could be captured it could then be transformed into hydrates and in principle stored deep in the ocean thus improving atmospheric conditions and slowing down the global warming effect (Haugan and Drange, 1992; Wolsky et al., 1994; Kobayashi and Sato, 1995; Lund, 1995; Holder et al., 1995; Brewer et al., 1999; 2000; Alendal and Draunge, 2001; Mori, 1999a). It is noted that CO_2 can also be found in the liquid state. In this case hydrate formation is also possible due to favorable temperature and pressure conditions.

Hydrates have been synonymous with problems in the oil and gas industry for decades. If water is transported with one of the over 100 known gases that can be a suitable guest molecule, and under the correct equilibrium conditions, hydrates may form. This can cause many problems in the transporting of oil and gas. Hydrate can form plugs in pipelines, which can block the pipeline and damage equipment such as pumps and compressors. Therefore, much research has gone into finding inhibitors, which increase the pressure at a given temperature at which hydrates will form. Such inhibitors include sodium chloride, glycol, and methanol (Sloan, 1998a).

At present, hydrate research is recognized as an important field due to the hazards and possibilities that gas hydrates pose. Fundamental studies on gas hydrates are needed in order to design safe, economical, and environmentally acceptable processes and facilities to deal with hydrate forming systems and to exploit in situ methane hydrate as a potential energy resource. The focus of this thesis is to provide fundamental experimental information relevant to thermodynamics, kinetics, and the morphology of gas hydrates where significant knowledge gaps exist. We work with methane, carbon dioxide, and ethane hydrates because the information gathered is useful in a number of technologies related to these hydrates as will be discussed in more detail later in this chapter.

1.1 GAS OR CLATHRATE HYDRATES

Clathrates usually consist of two molecular species, one physically entrapping the other by making up a cage-like structure containing cavities. There are two categories of clathrates, those where the cage or lattice like structure is made up of water molecules bonded together, and those built up by molecules other than water. The first group mentioned is known as clathrate hydrates or gas hydrates.

In a hydrate, the species forming the lattice is commonly called the host, while the caged component is called the guest. The host-lattice is created by water molecules connected together through hydrogen bonding. When the water molecules hydrogen bond they create cavities where the guest molecule can reside. The host-lattice is thermodynamically unstable without the presence of a guest molecule in the cavity. The guest molecule, which stabilizes the lattice, is held in place inside the lattice by weak attractive van der Waals forces. It is important to note that there is no physical bonding between the host-lattice and guest molecule, and that only one guest molecule is contained in each cavity. The guest molecule must have a diameter that is smaller than the cavity diameter, but not too small, and the guest molecule must not interfere with the hydrogen bonding of the lattice. Guest molecules such as helium, hydrogen and neon cannot (Sloan, 1998a) stabilize a hydrate lattice because their diameter is too small, generally a diameter less then $3.0 \stackrel{o}{A}$ is too small to stabilize a hydrate lattice.

Sloan proposed that the size ratio of the guest molecule to the cavity determines whether the guest can form a stable hydrate structure (Sloan, 1998a). In order to obtain a stable hydrate structure the ratio needs to be approximately 0.9. If the ratio is significantly less or above unity, stable hydrates structures will not be formed.

There are four known gas hydrate structures: structure I; structure II; structure H, and a recently discovered and yet unnamed structure (Sloan, 1998a; Ripmeester and Ratcliffe, 1990; Konstantin and Ripmeester 1999). Structure I consists of two different types of cavities. The first cavity is formed when water molecules hydrogen bond in such a way that they form a structure with 12 faces and 5 sides to each face called a pentagonal dodecahedron (5^{12}). When the pentagonal dodecahedron links together by their vertices it creates a second type of cavity, a polyhedron with 12 pentagonal and 2 hexagonal faces ($5^{12}6^2$) called a tetrakaidecahedron, which is larger than the dodecahedron, figure 1.1. This structure gives a unit cell consisting of six large $5^{12}6^2$ cavities, and two small 5^{12} cavities created by 46 water molecules. Only small molecules with a diameter between 4.2-6.0 Å, can form structure I hydrates. Common structure I forming gases are methane, ethane and carbon dioxide.

Structure II is formed when the pentagonal dodecahedron links together through face sharing, not by the vertices as in structure I (Sloan, 1998a). By linking together through face sharing, they create a hexakaidecahedron, a polyhedron with 12 pentagonal and 4 hexagonal faces. This cavity is larger than the large cavity in structure I, while the small cavity in structure II is slightly smaller than the small cavity in structure I because of the bending in the hydrogen bonding. Structure II hydrate consists of 16 small and 8 large cavities made up by 136 water molecules, see figure 1.2. Molecules forming structure II have a diameter in the range of 6-7 $\stackrel{\circ}{A}$. Some examples of structure II forming gases are propane and iso-butane. In addition, very small molecules like argon, krypton and nitrogen will form structure II due to the smaller size of the $5^{12}6^2$ cavity.

An important characteristic of structure I and structure II is that they only need one component entering the structure to make it thermodynamically stable. For example, small molecules like methane whose size would allow it to enter and stabilize the small cavities in structure I, will also enter the large cavity in the absence of a larger molecule. It is important to note that guest molecules whose size only allows them to fill the large cavity can still form structures I and II. Ethane is an example of a guest molecule that is too large to fill the small spaces in structure I, but will stabilize the hydrate by filling the large cavities, leaving the smaller ones empty. Gas-mixtures can also form structure I and structure II by filling the small and large cavities with different sized molecules.



Figure 1.1 Structure I hydrate cavities (adapted from Ripmeester and Ratcliffe, 1990)



Figure 1.2 Structure II hydrate cavities (adapted from Ripmeester and Ratcliffe, 1990)

Structure H was discovered in 1987 at the National Research Council of Canada (Ripmeester et. al, 1987). It differs from the two other structures because it is composed of three different kinds of crystal cavities, two of which are small and of comparable sizes, and one is a large non-spherical cavity. It is also unique compared to the two previous structures because it requires molecules of two different sizes to stabilize the crystal. Like structure I and structure II, structure H has the basic 5^{12} cage. The two other cavities consist of a $4^35^66^3$ cage which has three fairly strained square faces, six pentagonal and three hexagonal faces, and a large $5^{12}6^8$ cage made up of twelve pentagonal and eight hexagonal faces, figure 1.3. The latter cavity is the largest hydrate cavity of any of the structures and is estimated to fit guests up to 9 \mathring{A} in diameter. One unit cell of structure H can contain at most one large molecule, five small molecules and 34 water molecules. Another characteristic of structure H hydrate that makes it unique compared to the two other structures is that it is not enough for the large molecule in structure H to have the right size as for structure I and structure II, the shape and efficient

space filling is also important. Small molecules, known as help guests, such as methane, xenon or hydrogen sulfide, can occupy the two small cages in structure H, while intermediate sized hydrocarbons such as adamantane, cycloheptane or 2,2-dimetylbutane, also know as neohexane, can fill the large cavity of structure H. Experiments at the National Research Council of Canada showed that carbon dioxide with neohexane and ice form structure H hydrate. There could be serious implications for the use of carbon dioxide in secondary oil recovery if structure H hydrate forms in these systems. Hence, there is a need to know the structure H equilibrium hydrate formation conditions in methane, carbon dioxide containing system. One such system is that with neohexane which is studied in this work.



Figure 1.3 Structure H cavities (adapted from Ripmeester and Ratcliffe, 1990).

In 1999 another hydrate structure was reported at the National Research Council of Canada by Konstantin and Ripmeester (1999). This hydrate structure is extremely complex and exhibits bimodal guest hydration. It has not received much attention as of yet because it can only be formed when choline hydroxide is co-crystallized with tetra-npropylammonium fluoride from an aqueous solution. A detailed description of this new 5-caged hydrate structure is given by Konstantin and Ripmeester.

1.2 PHASE EQUILIBRIA

The majority of studies on hydrate equilibrium focus on the task of gathering incipient equilibrium hydrate formation data as well as developing predictive methods for the calculation of phase equilibria. Incipient hydrate formation conditions refer to the situation in which and infinitesimal amount of the hydrate phase is present in equilibrium with the fluid phases. The knowledge of equilibrium hydrate forming (pressure-temperature) conditions is necessary for the rational and economic design of processes in the various chemical fields of oil and gas as well as other industries where hydrate formation is encountered. An extensive account of hydrate phase equilibrium data for numerous components is given by Sloan (1998a).

1.3 KINETICS OF HYDRATE FORMATION

There are two fundamental questions that must be addressed when time is a consideration with respect to hydrate formation (Englezos, 1996). The first is the amount of time required in order for a hydrate to reach a critical size nucleus. The second is how fast the hydrate grows after the critical size nucleus has been achieved.

1.3.1 Nucleation

Hydrate nucleation refers to the process where hydrate crystals called nuclei, grow and disperse until they attain a critical size for continued growth. If the size of the nuclei is less than the critical size (Bishnoi and Natarajan, 1996), they are unstable and may continue to grow or break in the aqueous solution. If the growing nuclei reach the critical size they become stable, which leads to the formation of hydrate crystals. This period when the hydrate nuclei are forming and dissolving in a supersaturated solution to the time when the nuclei reach the critical size is called the induction time. The induction time is believed to be a stochastic phenomenon that cannot be predicted.

1.3.1.1 Factors Affecting Induction Time

The nucleation time has been found to depend on many parameters. It has been experimentally shown that in addition to temperature and pressure nucleation time depends on the previous history of the water (Vysnauskas and Bishnoi, 1984), degree of supersaturation (Bishnoi and Natarajan, 1996), stirring rate (Englezos et al., 1987), and the molecular diameter to cavity size ratio (Sloan, 1998a).

Vysnauskas and Bishnoi performed experiments that showed the effect of the history of the water on the induction time. They concluded that water from thawed ice or water from disassociated hydrates had the shortest induction times. This is due to the fact that the water retains memory and is more structured if it comes from a previously highly structured form such as ice or hydrates. Double distilled water was then shown to have quicker induction times than that of hot ordinary tap water, suggesting that the higher the purity of the water the more structure it exhibits.

Supersaturation is defined as the concentration of the dissolved gas in solution divided by the amount of dissolved gas corresponding to three phase equilibria. Natarajan et al. (1994) found that induction time increased with decreasing supersaturation, and that induction time decreased with increased supersaturation. They also made a suggestion that high supersaturation might mask the random nature of hydrate nucleation thereby making the time period of nucleation seem predictable, which is not what data for low supersaturation concludes. Nucleation times might also be masked by heterogeneities present in the experimental system, indicating that the hydrate nucleation process is truly stochastic. Earlier experiments by Barlow and Hayment (Sloan, 1998a), and Parent and Bishnoi (1996), suggest that nucleation time is a stochastic process.

The stirring rate was found to have a significant effect on the nucleation time (Englezos et al., 1987). The higher the stirring rate the shorter the induction times were. Other studies showed that higher turbulence gives rise to quicker induction times which supports the effect of stirring rate on induction time.

The guest molecule to cavity size ratio was studied by Sloan's group (Sloan, 1990). He proved that some guest molecules are better in stabilizing the hydrate structure because of their size. Sloan then concluded that the higher the stability the guest molecule provides the shorter the induction times are.

Finally, a hydrate equilibrium point is defined as the minimum pressure at a given temperature that hydrates can exist at indefinitely. Hence, the higher this pressure is above the equilibrium pressure at a given temperature the shorter the induction time. The same is true if you are at the equilibrium point and temperature is decreased. The colder

the temperature is from the equilibrium temperature the faster the nucleation will take place. These phenomena will be discussed in more detail later in the driving force for hydrate nucleation section.

1.3.1.2 Driving Force for Nucleation

Driving force for hydrate nucleation has been studied by numerous researchers who have all developed there own theories. Natarajan et al. (1994) defined the driving force for nucleation that is consistent with their definition of supersaturation in the nucleation region. Natarajan et al. defined the supersaturation or driving force for nucleation to be

$$\frac{f_i^{\exp}}{f_i^{eq}} - 1 \tag{1.1}$$

where f_i^{exp} is the fugacity of the dissolved gas i at the experimental temperature (T^{exp}) and pressure (P^{exp}) conditions and f_i^{eq} is the fugacity of gas i at the three-phase (vapor-liquid-hydrate) equilibrium conditions (P^{eq}, T^{exp}). P^{eq} is the three-phase hydrate equilibrium formation pressure at T^{exp}. This implies that in accordance with supersaturation, the induction time decreases with increasing supersaturation, and increases with decreasing supersaturation.

Other suggested driving forces include that of Vysniauskas and Bishnoi (1983), Skovborg et al. (1993), and Sloan and Christiansen (Sloan, 1998a). These driving forces are given below in table 1.1 along with a plot of supersaturation vs. induction time in figure 1.4. Vysniauskas and Bishnoi suggested that the driving force is equal to the

Investigator	Vysniauskas and Bishnoi (1983)	Skovborg et al., (1993)	Natarajan et al. (1994)	Sloan and Christiansen (1998a)
Driving Force	$T^{eq} - T^{exp}$	$\mu_{wH}^{\exp} - \mu_{wL}^{\exp}$	$\frac{f_i^{\exp}}{f_i^{eq}} - 1$	$\Delta g^{ ext{exp}}$

Table 1.1 Driving Forces For Nucleation Reported in Literature

deviation of the experimental temperature (T^{exp}) to the equilibrium temperature (T^{eq}) at a given experimental pressure that hydrates are in three-phase equilibrium (vapor-hydrateliquid). This is also called the subcooling. Skovborg et al. define the driving force to be the difference in the chemical potential of water in the hydrate phase (μ_{wH}^{exp}) at the experimental conditions to water in the liquid state (μ_{wL}^{exp}) at the experimental conditions. Sloan and Christiansen use an expression based on the change in molar Gibbs free energy (Δg^{exp}) as the driving force for hydrate nucleation.



Figure 1.4 Effect of driving force or supersaturation on induction time (adapted from Natarajan et al., 1994).

A correlation by Natarajan et al. (1994) was developed in order to estimate the onset of nucleation based on figure 1.4. They arrived at the following equation for the induction time t_{ind}

$$t_{ind} = K \left(\frac{f_g^{\nu}}{f_{eq}} - 1\right)^{-m}$$
(1.2)

where f_g^{ν} is the fugacity of the gas at the experimental temperature and pressure (T^{exp}, P^{exp}) and f_{eq} is the fugacity of the gas at the experimental temperature and three-phase equilibrium pressure (T^{exp}, P^{eq}). *K* and *m* are fitted parameters depending on the hydrate forming gas and are given by Natarajan et al. for carbon dioxide, ethane and methane.

1.3.2 Hydrate Crystal Growth

Hydrate growth is the process where the hydrate nuclei have achieved the critical size and continue to grow and form hydrate crystals. The growth process depends on mass and heat transfer, as well as the factors that affect hydrate nucleation which have already been discussed. A comprehensive model that incorporated crystallization theory was developed at the University of Calgary (Englezos et al., 1987).

The above-mentioned model is a mechanistic one with only one adjustable parameter per hydrate former. The nucleus is assumed to form instantaneously by primary nucleation. The driving force for the hydrate crystallization process is the difference in the fugacity of the dissolved gas, f, and the three-phase equilibrium fugacity, f_{eq} , at the experimental temperature. As seen the driving force is determined

$$\Delta f = f - f_{ea} \tag{1.3}$$

by the deviation from the three-phase equilibrium, vapor-liquid-hydrate, conditions and not the magnitude of the experimental pressure.

A common method to monitor hydrate kinetics is based on measuring the amount of hydrate forming gas consumed as a function of time (Englezos et al. 1987). Another method was pioneered by Makogon in 1974 and is based on crystal thickness measurements coupled with morphology (Makogon, 1997). Morphological studies reveal important mechanistic aspects of hydrate systems and will be discussed in detail later in this chapter. *Due to their importance, such studies are also included in this thesis*. Recently, Raman spectroscopy has been employed to provide kinetic spectra describing the transition from dissolved methane-to-methane hydrate (Sloan, 1998b). X-Ray diffraction has also been implemented for carbon dioxide hydrates (Takeya, 1999).

Techniques based on light scattering have been examined by Nerheim et al. (1992), Monfort and Nzihou (1993), Bylov and Rasmussen (1996), and Parent (1993) in order to monitor the kinetics of hydrate growth, but have not shown consistent results. Measuring the rate of growth from hydrate nuclei using light scattering techniques is difficult due to the extremely small sizes of these nuclei. *An alternative technique will be proposed in this work to exploit light scattering*.

1.3.3 Measurement of Gas Consumption

A typical gas hydrate formation curve obtained during hydrate formation from CH₄ and water is shown in figure 1.5. It shows the total moles of hydrate forming gas consumed during an experiment at constant temperature and pressure in a semi batch vessel.



Figure 1.5 Moles of gas consumed vs. time in a kinetics of hydrate formation experiment (adapted from Englezos et al., 1990)

In figure 1.5, the onset of hydrate formation occurs at the nucleation point, B, which is known as the turbidity time. The turbidity time denotes the first appearance of stable hydrate crystals and is the beginning of the hydrate growth phase. n^* is the

number of moles of methane gas corresponding to a vapor-liquid water equilibrium. This equilibrium is hypothetical because hydrates form at these conditions. This would be the solubility of methane in water in the absence of hydrates. n_{eq} is the number of moles of methane dissolved in liquid water corresponding to a vapor-liquid-hydrate equilibrium pressure at the system temperature. At the system temperature this is known as the incipient equilibrium hydrate formation pressure, P_{eq} . The value of n_{eq} is less then n^* in the hydrate formation region because it corresponds to a lower pressure. It was hypothesized that the difference in moles of gas between point B (n_B) and n_{eq} accounts for the amount of gas consumed in the formation of hydrate nuclei as postulated by Englezos et al. (1987). In order to validate this assumption experiments on solubility of the hydrate forming gas in the presence of hydrates must be performed. Moreover, the amount of dissolved gas in equilibrium with hydrate is an important parameter to be known when considering the discharge of CO₂ into the ocean or studying methane solubility in natural waters in connection to hydrate formation.

1.4 SOLUBILITY OF GASES IN WATER IN THE PRESENCE OF HYDRATES

Ohmura and Mori (1999) have reviewed the literature concerning solubility of CO_2 in the presence of CO_2 hydrates and have found that the limited experimental data available exhibits contradictory results between different research groups, figure 1.6. Two studies conducted using water (Yang et al., 2000; Yamane and Aya, 1995) and one performed with seawater (Kimuro et al., 1994) concluded that the solubility of carbon dioxide gas in water with hydrates decreases with decreasing temperature in the hydrate

formation region. On the other hand, experiments carried out by Teng and Yamasaki (1998) and Stewart and Munjal (1970) show contradictory results.

Referring back to figure 1.5 the solubility of the gas dissolved in equilibrium with its hydrate was hypothesized to be equal to n_{eq} . n_{eq} is the number of moles of methane dissolved in liquid water corresponding to a vapor-liquid-hydrate equilibrium.



Figure 1.6 Solubility of CO₂ in Sea Water (adapted from Ohmura and Mori, 1999)

Ohmura and Mori concluded that the solubility of CO_2 in water in the hydrate formation region should decrease with decreasing temperature. This is in agreement with theoretical calculation of the solubility of hydrate forming gases in the presence of hydrates (Yang et al., 2000; Zatspina and Buffet, 1997; Tabe et al., 1998; Englezos and Bishnoi, 1988). Ohmura and Mori also expressed the need for more effective experimental techniques to be used to investigate and find the true trend of solubility as a function of temperature in the hydrate formation region. *Therefore, it is necessary to devise a reliable technique in order to measure gas solubility in the presence of hydrates and to clarify the literature on how the solubility is affected by temperature in these conditions.* Furthermore, the assumption made by Englezos et al. (1987) and discussed in section 1.3.3 will also be tested.

1.5 CRYSTAL MORPHOLOGY

This section is concerned with the study of crystal morphology on gas hydrates. It is broken down into the following three sections (1) observations (2) modeling and growth measurements and (3) the measurement of mechanical properties.

1.5.1 Observations

Makogon was the first researcher to extensively report the morphology of hydrate phases present and growing (Makogon, 1981). Makogon used a rectangular, windowed container to demonstrate many different variations in the morphology of hydrate crystals. The reported crystals included thread like, spherulitic, film-like, dendritic, viscera-like, among other geometries which are accredited to many factors. These factors included the variation in hydrate forming gas, the super cooling, the experimental pressure, and the location of hydrate nucleation. Makogon also assumed that independent of the crystal morphology, the diffusion of hydrocarbon molecules through a hydrate layer sustained the hydrate growth over the entire gas-hydrate-water interface.

Other earlier studies included those of Maini and Bishnoi in 1981 (Maini and Bishnoi, 1981) and Topham in 1984 (Topham, 1984). Both groups of investigators

reported their observations of clathrate hydrate formation on methane bubbles or simulated natural gas released in a down flow of seawater in a simulated deep sea environment. Their observations suggested that hydrates formed on the bubble and continued to grow until the bubble was entrapped in a hydrate layer. The bubble surface then became rigid in shape but remained quite flexible. Another observation made was that flakes of hydrate from the rear of the bubble broke free and separated entirely.

In the late 80's and early 90's, Mori's group studied liquid fluorocarbons (CFC-12, HFC-134a) systems that would form hydrates in the presence of water (Mori and Mori, 1989a,b; Isobe and Mori, 1992). In their experiments, the liquid fluorocarbon was injected continuously into a pool of water to vaporize the liquid fluorocarbon while cooling the surrounding water. They observed the formation of hydrates on the surface of the fluorocarbon bubbles (gas phase) while it was rising in the pool of water and/or resting at the free surface of the water pool.

According to Sugaya and Mori (1996), Aya et al. (1993) and Shindo et al. (1993) who placed CO_2 drops on a solid plate and a wire grid, respectively, immersed in quiescent water or seawater not saturated with CO_2 . Their experiments where performed at pressures corresponding to depths of 3 km (30 MPa) in seawater. Both researchers observed immediate formation of a thin, smooth, semi-transparent hydrate film all over the surface of each drop. Both also concluded that hydrate coated drops shrank with the passing of time at rates appreciably lower than those for uncoated drops.

Later, Nojima and Mori (1994) studied (CFC-11, HFC-141b) hydrate-forming fluorocarbons systems. In these experiments one bubble (gas phase) of fluorocarbon was held virtually stationary in a down flow of water. The hydrate first appeared on the

surface of each bubble in the form of tiny particles. The tiny particles were swept to the back of the bubble and accumulated until a hydrate layer surrounded the entire bubble. These observations are consistent with earlier reported morphological observations (Maini and Bishnoi, 1981; Topham, 1984). Nojima and Mori (1994) also noted that the hydrate bubble was so fragile that it would crumble with time due to the hydrodynamic shear imposed by the down flow of water. Another interesting observation by Nojima and Mori was that they observed that the shrinkage of bubbles occurred more rapidly on hydrate free surfaces than on hydrate-covered bubbles. Concluding that the hydrate covering is porous and does not impede the rate of dissolution of fluorocarbon into the water. This observation is in disagreement with work by Shindo et al. (1993), who observed much more rapid shrinkage in hydrate free CO₂ droplets.

More observational studies were carried out by Sugaya and Mori (1996) on the boundary of (HFC-134a;CF₃CH₂F) fluorocarbons in the vapor or liquid state and water. Their studies were carried out on droplets (4.5-6.5 mm, measured from paper using given scale) of the fluorocarbon as well as planar interfaces between the fluorocarbon and water. They observed that the degree of supersaturation of the water phase with the fluorocarbon strongly influences the surface morphology of the formed hydrate layer. The mechanical structure of the hydrate layer was independent of whether the fluorocarbon was in the vapor or the liquid state but was strongly dependent on the hydrodynamic conditions near the interface. Observations of the shrinkage rate on fluorocarbon droplets were also in agreement with Shindo et al. (1993). They concluded that the hydrate layer formed on the surface of a fluorocarbon drop held stationary is not

as porous as the coagulation of hydrate particles observed on the surface of buoying fluorocarbon-vapor bubbles (Nojima and Mori, 1994).

Sugaya and Mori (1996) conducted their experiments on flourocarbon droplets in the presence of saturated and not saturated water. Their findings indicate that the hydrate phase grows quickly on the surface of each drop, till it extends all over the entire surface. The surface morphology established in the early process, several seconds, is maintained thereafter if the surrounding water is saturated. If the surrounding water was not saturated the initial morphology faded out quickly, reforming the surface all over the hydrate shell to be of smooth and fine texture. After extended periods of time the hydrate-coated drop subsequently shrinks in the medium of unsaturated water, showing no sign of undulation or buckling of the shell but keeping a smooth surface throughout. They postulated that the hydrate shell kept a smooth surface while shrinking due to the continuous and simultaneous renewal and decomposition of hydrate on the shell.

Mori and coworkers (Ohmura et al., 1999) continued their work on the growth and dissociation of clathrate hydrate crystals in liquid water in contact with a hydrophobic hydrate forming liquid. The liquid-hydrodchlorofluorocarbon was R-141b, which is known to form structure II hydrate. The experiments were carried out either with pure water or presaturated water, which was in contact with R-141b at about the three-phase equilibrium temperature (Experiments were done with varying degrees of subcooling). They observed that presaturated water at high subcooling (~6.5 K) exhibited two stages of hydrate-crystal growth. These two stages varied not only in crystal morphology but the length of time was also greatly different. The first stage was characterized by lateral crystal growth of a thin, fine-grained polycrystalline layer along

the R-141b surface and was observed for several tens of seconds. The later stage began typically with a delay of 10 min and continued for a few tens of hours. The later stage exhibited radial growth of plate-like crystals standing upright on the outer surface of the drop-enclosing hydrate shell formed in the first stage. An increase in temperature below the three-phase temperature produced the dissolution of the plate like crystal, which left the hydrate shell apparently unchanged. It is important to note the later stage was never observed in the presence of pure water and/or small subcooling (~ 2 K).

Kato et al. (2000) carried out experiments to investigate the drop formation behaviour of a hydrophobic hydrate-forming liquid, HCFC-141b (CH3CCl2F), at a single nozzle in a water stream under hydrate-forming thermodynamic conditions. Their attention was focused on the relationship between the clathrate-hydrate formation and drop formation. They observed two discrete hydrate crusts growing along the liquidliquid interface. One forms a frontal cap and the other forms a cylindrical root on each growing drop before its detachment from the nozzle. Most of the latter crust remains at the tip of the nozzle after the detachment of the drop so that it grows into a bell-shaped or nearly cylindrical funnel composed of hydrate deposits in the course of successive growth/detachment of drops. The size of these drops is dependent on the instantaneous diameter of the hydrate-funnel tip rather than the diameter of the nozzle itself. Thus, the size of the drops successively released into the water stream generally varies synchronously with quasi-periodical alternation of growth and breaking of the hydrate funnels. The growth and breaking of the hydrate funnels and the resultant drop-size variation are significantly dependent on the system temperature (or the system subcooling

from the liquid/liquid/hydrate equilibrium temperature), the nozzle diameter, and the velocity of the drop-forming liquid through the nozzle.

1.5.2 Modeling and Growth Measurements

Mori and Mochizuki (1996; 1997) developed a model to account for the mass transfer across clathrate hydrate films. The assumptions given by their model are listed below. Each hydrate film is assumed to be a solid plate intervening between a guest-fluid phase, in which water is insoluble or already dissolved to saturation, and a liquid water phase in which the guest species is dissolved to form a steady, spatial variation of the mole fraction of the guest species from the solubility at the hydrate-liquid water interface to the solubility in the bulk liquid phase. The hydrate film is uniform and constant in thickness. Microperforations are evenly distributed over its full width and are approximated by tortuous capillaries having the same constant radius and the same length. Except for the capillaries the hydrate layer is impermeable to both water and the guest species. Liquid water permeates the hydrate film, filling the capillaries. The driving force for pulling the water in is the capillary pressure induced by the water/guestfluid side due to the hydrophilic nature of the hydrate surface. Hydrate crystals are continuously formed at or near the interface, thus compensating the dissociation in progress at the water-phase-side surface of the hydrate film. A portion of the guest molecules released from the dissociating hydrate crystals at the water-phase-side film surface are pulled into the capillaries, being dissolved in the liquid water. The rest of the released guest molecules are transferred into the bulk of the water phase. The water filling the capillaries is saturated with the guest species. Neither formation nor

disassociation of the hydrate occurs inside each capillary except for the immediate vicinity of its mouths.

The formation and dissociation of the hydrate crystals occur simultaneously on the opposite surfaces of the hydrate film, and are both rate-controlled exclusively by relevant mass transfer processes. The formation is controlled by the rate of water permeation through the capillaries. The dissociation is controlled by the rate of diffusive or convective removal of the guest molecules from the water-phase-side surface. The solubility of the guest molecule in water at the hydrate-liquid water interface is the solubility of the guest molecule in water in equilibrium with its hydrate.

Their model given in Mori and Mochizuki (1997) gives valuable information to the how certain factors relate to the growth of a hydrate film. They found that the thickness of the film was inversely proportional to the mass transfer coefficient on the waterside of the film. This is inherently dependent on the flow of water relative to the film. They also noted that the film tends to be thicker as the internal texture becomes coarser.

A search for the mechanism of CO_2 dissolution being retarded through the hydrate film into the surrounding water was investigated by Mori and Mochizuki (1998). The researchers suggested three different mechanisms. (a) The loss of drop-surface mobility due to the hydrate film formation, this led to the decrease of the convective mass transfer coefficient for CO_2 in the water phase. (b) An increase and decrease in the effective viscosity and the mass diffusion coefficient, respectively, in the water phase due to the discharge of structured clusters from the hydrate film surface. This causes a decrease in the mass transfer coefficient for CO_2 in the water phase. (c) The reduction in solubility of
CO_2 in liquid water in thermodynamically stable hydrate/liquid water coexisting conditions at a temperature below the three-phase equilibrium temperature at a given pressure. This decrease in solubility causes a smaller driving force for the diffusive, or convective, CO_2 transfer from hydrate-film surfaces to the adjoining liquid water phase compared to that for the transfer from hydrate-free CO_2 -water interfaces. They deemed that the latter was the most dominant mechanism.

The modeling of the clathrate hydrate formation at the interface between liquid CO_2 and water phases was reviewed by Mori (1998). He found that the eight different models had been employed up to 1997 on the formation and metabolic self-preservation of a hydrate film at the interface along with the mass transfer of CO_2 across this hydrate film. Mori critically reviewed all the models and differentiated between them, pointing out the weakness, if any, in the physical or mathematical formulation. The model of Mori and Mochizuki (2000) is the most recent, as well as the first to take into account heat and mass transfer effects and will be discussed later on in this review.

The first attempt at simultaneously modeling the heat and mass transfer to/from and across a hydrate film is credited to Mori and Mochizuki (2000). Mori and Mochizuki extended their water-permeable film model (Mochizuki and Mori, 1997) to describe steady or quasi-steady, one-dimensional, simultaneous heat and mass transfer. They took into account the exothermic hydrate formation and endothermic hydrate dissociation within the confines of a hydrate film. In their simulation they recognized that the effect of advection of the hydrate crystals and liquid water inside hydrate films practically arises, resulting in more or less curved temperature profiles inside the hydrate films, only when these films are highly porous and water-permeable.

Mochizuki and Mori (2000) focused their efforts on numerical simulation of transient heat and mass transfer controlling the growth of a hydrate film. They described a simulation of the asymptotic process of growth, or thinning, of a hydrate film which is assumed to be formed instantly at the phase boundary between liquid water in steady convection and a quiescent guest fluid extending to a finite thickness. They assumed that the three-phase system is uniform over the lateral extent of the hydrate film in order to formulate the film growth (or the film thinning) process in the framework of onedimensional heat and mass transfer with moving boundaries. Their first simulation neglected the water-permeation limit throughout the calculations in order to maximize the rate of heat removal. They noted that these predictions that yielded film thickness of 0.4 mm within a few minutes was not in good agreement with experimental results of the order of 10 µm (Uchida and Kawabata, 1997; Sugaya and Mori, 1996). Mochizuki and Mori concluded that the mechanism of heat removal does not dominate the rate of hydrate formation. In other simulations they concluded that the dominant mechanism for controlling the rate of hydrate formation is water permeation. They also stated that heat removal could be neglected when dealing with hydrate films no thicker then 0.3mm. Another important observation that came about by their modeling was that the direction of heat transfer between the hydrate film and the guest-fluid phase is reversed in the course of the film growth. They found that the first couple seconds, the heat generated by the hydrate formation at the guest-fluid-phase surface was entirely transferred to the opposite surface. A substantial portion of this heat is used to dissociate the hydrate, while the residual of the heat is convected away into the water phase.

Using a laser interferometer having a resolution of approximately 1 μ m, Ohmura et al. (2000) directly measured the thickness of clathrate-hydrate films at the planar interface between a liquid hydrofluorocarbon, R-134a (CH2FCF3), and liquid water. The interferometer measured the film thickness of a hydrate film formed with either pure water having no prior contact with R-134a or water presaturated with R-134a. A series of intermittent measurements was made until the film was aged up to 150 hours. For hydrate films formed with pure water held at a large subcooling (approximately 7 K) below the triple (liquid-R-134a/hydrate/liquid-water) equilibrium temperature, the initial thickness was similar to 10 µm. This thickness was maintained for a few tens of hours; then it gradually increased, reaching similar to 30 µm 100 h after the film formed. With pure water at a smaller subcooling (less than or approximately equal to 2 K), the thickness of hydrate films was initially as large as approximatley 80 µm; it rapidly decreased to 15-20 μ m and then increased to 30-40 μ m 150 h after the film formed. With presaturated water at small subcoolings (less than or approximately equal to 6 K), each hydrate film was a mosaic of polygonal hydrate crystal plates. Each plate was several millimeters wide and 20-170 µm thick. No measurement could be made with presaturated water at a large subcooling (greater than or approximately equal to 6 K) because of sword-like hydrate crystals that have grown in crowds into the water phase from the hydrate film surface.

Mori (2001) found that the lateral growth of polycrystalline clathrate-hydrate films along the interface between liquid water and a hydrate-forming substance in the state of a liquid or a gas is considered to be rate-controlled by the transfer of heat of hydrate formation from the edge of each film to the surrounding, i.e., the water and hydrate-former phases. A simple convective-heat-transfer model is presented, which

predicts the product of lateral growth rate of a film and its thickness to be proportional to the 3/2 power of the effective temperature driving force. The application of the model to the existent experimental data on the growth of CO₂-hydrate films leads to a rough estimation of their initial thickness, 0.3-0.6 μ m.

1.5.3 Measurement of Mechanical Properties

Mechanical properties have also been of interest in hydrate research. These properties are not a focus of this work, therefore a detailed review of this topic was not performed. Measurements of mechanical properties of the liquid CO_2 -water- CO_2 hydrate system was made by Uchida and Kawabata (1997). They measured the interfacial tensions and the hydrate film strength. Their experiments were performed on hanging drops of CO_2 . They observed that the interfacial tension between liquid CO_2 and water decreased slightly as the temperature was raised from 266.3 to 284.9 K. The average interfacial tension was reported to be 29 dyn-cm⁻¹. Other measurements indicated that the sums of the interfacial tensions between liquid CO_2 and CO_2 -hydrate film and between CO_2 -hydrate film and water were about 26% less that between liquid CO_2 and water. They also observed that the strength of the hydrate film was dependent on the hydrate film thickness.

Ohmura et al. (2000) investigated the mechanical properties of water/hydrateformer phase boundaries and phase-separating hydrate films. In particular they investigated the liquid-liquid interfacial tension before the formation and after the dissociation of each hydrate film, and the membrane force working in the hydrate film during its complete covering of the phase boundary. They found that the surface tension

decreased with the formation of hydrates and decreased the baseline value in the absence of hydrates. Therefore there was no memory effect as this process was repeated several times with no notable change. They also concluded that membrane forces exhibit no particular pattern of chronological change.

1.5.4 Concluding Remarks

Morphological studies reveal important information about the mechanistic aspects of hydrate nucleation, growth, and decomposition. As can be seen in the literature review, most of the experimental studies on crystal morphology have been focused on carbon dioxide in the liquid phase and fluorocarbons in the liquid or vapour phases in the presence of water. Crystal morphology experiments in the past have also been limited to monitoring one droplet at a time. In this study we conduct crystal morphology experiments on stagnant water droplets in the presence of CH_4 or CO_2 gas. The bulk phase in previous experiments is also pure water or seawater but in our experiments water droplets will be present in a gas atmosphere taking up the majority of reactor volume. These experiments are not only unique in the selection of the phase of the hydrate former gas but in the sense that observations will be made simultaneously on multiple, up to 3, droplets in a viewing area and/or of different droplet diameter.

Experiments will be performed in a crystallizer where liquid droplets of water will be placed in contact with high pressure CH_4 or CO_2 under hydrate forming conditions. *After each experiment has run its course, hydrates will be decomposed by maintaining the pressure at 10 % below the three-phase equilibrium pressure.* The observed

decomposition along with the crystal morphology associated with decomposition will be monitored.

1.6 TECHNOLOGICAL ASPECTS

Ever since the discovery that natural gas and water can form gas hydrates and plug pipelines at temperatures above the freezing point of water, scientists have tried to find methods and chemicals that prevent hydrate formation. Hydrate prevention has become a major concern since the 1930's and has led to a large amount of research being conducted on the phase behavior of hydrate forming systems. Gas hydrate formation has also been recognized as an opportunity to develop useful applications. Gas hydrates that occur naturally in the earth's surface and in the depths of the ocean floor present a future energy source given the proper economic circumstances. In the following sections the benefits and opportunities related to methane and carbon dioxide gas hydrates will be discussed.

1.6.1 Methane

An important discovery was made in the 1960's by two Russian researches, Chersky and Makogon (Makogon et al, 1972). These two researchers discovered that gas hydrates, containing mostly methane, can be formed naturally in the earth. Today, it is known that natural gas hydrate exists in vast quantities within and below the permafrost zone and in sub sea sediments (Sloan, 1998a; Makogon, 1997). The amount of organic carbon entrapped in hydrate exceeds all other reserves (fossil fuels, soil, peat, and living organisms) (Suess et al., 1999). Naturally occurring methane hydrates are being looked upon as a future energy source and a potential global climate hazard if the entrapped gas is released into the atmosphere (Englezos, 1993; 2001).

Another benefit of CH_4 hydrates deals with the transportation and storage of natural gas. In the literature Khokhar et al. (1998) have demonstrated that economically it is more feasible to transport methane in hydrate form than cryogenically cooling or compressing methane. The storage potential of CH_4 in hydrate form is also a very promising alternative (Khokhar et al., 2000).

Feasibility studies have shown that storing and transporting natural gas as hydrates saves cost of approximately 24% when compared to methods such as liquefied natural gas (LNG) (Khokhar et al., 1998). A schematic comparison of natural gas storage as hydrate to conventional methods in shown in figure 1.7.

It has been shown that about $160m^3$ of natural gas can be stored as hydrate form under a volume of $1m^3$. Some applicable methods for storage include: keeping the hydrates under low temperature, or under high pressure. However, the concern is to obtain feasible and flexible methods for the production of hydrates.

$$160m^{3} @ \text{STP} \xrightarrow{-160^{\circ}C} Liquified NG$$

$$160m^{3} @ \text{STP} \xrightarrow{200bar} Compressed NG$$

$$\xrightarrow{10-25bar} 5-15^{\circ}C \rightarrow Hydrate$$

Figure 1.7 Natural gas storage conditions (adapted from Khokhar et al., 1998).

Methane can be stored as a structure I hydrate because it will occupy the small cage (5^{12}) . However, high formation pressures are required. In order to reduce this

pressure requirement, a miscible molecule like ethylene oxide can be used to fill the large cage $(5^{12}6^2)$ in the structure I hydrate. The same technique can be applied to structure II hydrates, but using tetrahydrofuran to fill the large cage $(5^{12}6^8)$, so that methane occupies the small cages. In a similar manner, the structure H hydrate can be treated with a large molecule such as 2,2-dimethyl butane to stabilize the large cavity $(5^{12}6^8)$, and having methane to occupy the smaller 5^{12} and $4^35^66^3$ cages (Khokhar et al., 1998). In addition, the formation of this structure takes place at lower pressures compared to the previous two structures.

Table 1.2 shows the comparison of methane storage in all three hydrate structures by occupying only the small cages and having a large molecule occupying the large cages. The maximum gas volume at STP contained in a single unit volume of hydrate is shown in column 2. From table 1.2 it can also be noticed that structure H hydrates have smaller unit structure sizes compared to structure I and structure II hydrates.

Table 1.2 Calculated maximum methane storage potential in the small cavities of all three structures by stabilizing the large cavity with a large molecule by Khokhar et al. (Khokhar et al., 1998).

Small cages for CH4	<i>Vol. of CH</i> ₄ (m ³)	Energy density* (kcal/m ³)	Unit cell size (A^3)
SI	56.02	5.32x10 ⁵	1728
sII	154.08	1.46×10^{6}	5177
sH	200.93	1.90×10^{6}	133
LNG @ -160 °C	600.0	6.00x10 ⁶	

*Energy density is defined as the energy of methane entrapped per unit volume.

It is important to take into account the drawbacks to such an approach of storing and transporting methane gas in hydrate form. The first point that should be addressed is how much methane can be recovered and the efficiency of such a recovery. Secondly, how much water will be required in order to capture a given amount of methane? In other words what is the maximum conversion of water to hydrate in the presence of methane at given temperatures and pressures? Then there is the question of separating neohexane from the water and vapor phase and how much of the neohexane can we recover? Finally we need to look into the transportation of these hydrates and the necessary equipment and material required in order to ensure safe delivery.

Economical investigations have been performed on the feasibility of storage and transportation of methane in hydrate form versus the technique that uses liquefied natural gas. Reports suggest that savings would be in the proximity of 24% if natural gas was transported in hydrate form instead of liquefied natural gas form (Khokar et al., 2000). Work is also under way by Mahajan et al. (2000) to develop an economical, energy efficient pathway to transport gas hydrates via the Gas to Liquid (GTL) scheme approach. GTL involves the initial conversion of natural gas to synthesis gas via partial oxidation or steam reforming. In a subsequent step the synthesis gas is catalytically converted to Fischer-Tropsch liquids and transported at room temperature.

1.6.2 Carbon Dioxide

One of the most common emissions from fossil fuel stacks is carbon dioxide (Wolsky et al, 1994). Carbon dioxide is a harmful green house. An important problem facing the environment today is the amount of greenhouse gases emitted into the atmosphere. If we could find economical ways to separate the carbon dioxide from the exhaust stream of fossil fuel stacks and dispose of it safely this could alleviate or slow down the global warming effect.

It has been known since the late 1800's that CO₂ is a suitable guest molecule that can physically combine with water under the proper temperature and pressure to form gas hydrates (Englezos, 1992). Two main reasons for studying CO_2 hydrate are the oil and gas industry and CO₂ sequestration. In the past CO₂ was also used as a means for water desalination and effluent concentration (Englezos, 1993). CO₂ and water are often found together in natural gas streams and are also found in oil reservoirs as a part of enhanced oil recovery. Hydrate formation in these environments may cause complications in extracting natural gas (Englezos, 1993). CO₂ also contributes to global warming (Wolsky et al., 1994). This is why scientists and engineers are exploring the option of sequestering CO₂ in the deep ocean (Brewer et al., 1999; Brewer et al., 2000; Alendal and Draunge, 2001; Mori, 1999). Finally, It should be noted that the natural uptake of CO₂ from the atmosphere by the ocean occurs on an enormous scale, and the ocean offers the world's most powerful long-term buffer against the rise of both temperature and CO_2 emissions (Brewer et al., 1999).

1.7 RESEARCH OBJECTIVES

Much work has been presented in the literature in order to prevent hydrate formation. In the last couple decades however, hydrates have been viewed as a valuable energy resource, a cost effective alternative of transporting and storing natural gas, and a possible way of safely removing harmful carbon dioxide emissions and depositing of them in the ocean.

This thesis will focus on gathering fundamental equilibrium, kinetic, and morphology information to fill in significant knowledge gaps in the literature and

advance our understanding of the hydrate formation process. This information is generally useful for the design of safe, economical, and environmentally acceptable facilities and process. These facilities and processes are related to the formation, recovery, storage, and transportation of methane hydrates and the formation and storage of carbon dioxide hydrates in the ocean. Model systems are utilized so that the results have broad applicability.

The research objectives of this thesis are as follows:

- Measure the solubility of CH₄ and CO₂ dissolved in liquid water in equilibrium with its hydrate. This work is expected to remove the controversy from the literature with respect to the solubility trend. It will also test the assumption made by Englezos et al. (1987) and in general provide an important piece of information for the onset of hydrate formation.
- Collect equilibrium hydrate formation data on CH₄ and CO₂ in the presence of neohexane and water. CH₄ is known to participate in structure H hydrate with a number of heavier compounds. It is also important to determine if CO₂ would form structure H with neohexane liquid and water. Such information is useful in considering hydrates for natural gas storage and transportation.
- Test a new kinetic study technique based on a new concept of growing hydrate crystals on suspended particles of known size, size distribution and charge. Ethane is chosen as a model system. This technique will employ dynamic light scattering. This information coupled with molecular level information from Neutron Scattering, Raman Spectroscopy, and X-Ray diffraction will aid in the refinement of existing kinetic models as well as the development of new models.
- Conduct morphological studies on structure I hydrate (CH₄-water & CO₂-water) and on structure H hydrate (CH₄-neohexane-water) to reveal the mechanistic aspects of hydrate nucleation, growth and decomposition.

Chapter 2

EXPERIMENTAL APPARATI AND PROCEDURE

A hydrate equilibrium apparatus at the University of British Columbia and its modifications and upgrades to increase its capability and versatility is described together with the relevant experimental procedures. In addition, the modifications of a laser light scattering apparatus at the University of Calgary and experimental procedure are also given.

2.1 HYDRATE APPARATUS

A hydrate phase equilibrium apparatus existed at the University of British Columbia when I started my studies (Englezos and Ngan, 1994). It consisted of a high pressure cell shown in figure 2.1. The cell was immersed in a temperature-controlled





bath as shown in figure 2.2.



Figure 2.2 Hydrate Equilibrium Apparatus (Englezos and Ngan, 1994)

The heart of the hydrate phase equilibrium apparatus is a high-pressure equilibrium cell, a 316 stainless steel vessel that is immersed in a temperature-controlled bath. The cell has two circular viewing windows on the front and back. Mixing of the cell contents is accomplished using a magnetic stir bar that is magnetically coupled to a set of rotating magnets (Tormag Engineering, Vancouver, B.C.) placed directly underneath the cell. The set of magnets is driven by an electric motor. The temperature at the top, middle and near the bottom inside the cell is measured by three Omega copper-constantan thermocouples with a \pm 0.10 K accuracy. The pressure is measured by a Bourdon tube Heisse pressure gauge with a range of 0-14 000 kPa and an accuracy that is believed to be less than 0.25 percent of the span.

2.1.1 Upgrade of the Phase Equilibrium Apparatus to measure gas phase composition

In order to measure the phase equilibrium of gas mixtures in solution with water under hydrate forming conditions, one must note the temperature, pressure as well as the composition of the species in the hydrate equilibrium cell. Modifications were then necessary to obtain gas phase concentrations of CH_4 and CO_2 in equilibrium with water and their coexisting hydrate.



Figure 2.3 Hydrate Equilibrium Apparatus (Servio et al., 1999)

The first modification was the addition of a Varian CX 3400 Gas Chromatograph (GC), which was connected on-line with the equilibrium cell and automated with a PC. A sampling bomb was then placed between the GC and the equilibrium cell. The purpose of the sample bomb was to allow a gas sample to be taken and the experimental pressure and temperature to be flashed to atmospheric pressure and room temperature before

injection into the GC. All lines from the GC to the equilibrium cell along with the pressure bomb were evacuated with the aid of a vacuum pump prior to gas analysis. The apparatus used to measure CO_2 , CH_4 hydrate equilibrium is show in figure 2.3

2.1.2 Experimental Procedure

Hydrate Equilibrium experiments are carried out using the isothermal pressure search technique (Englezos and Ngan, 1994). It involves keeping the temperature of the contents of the equilibrium cell constant while the pressure is varied until the equilibrium point is found. The equilibrium point is the minimum pressure at a given temperature that hydrates can exist at. The isothermal pressure search method is used for the simple fact that when a pressure change is imposed, the system can reach thermal equilibrium faster compared to the time required for an adjustment of the temperature.

The gas for analysis is transferred from the equilibrium cell to an evacuated pressure bomb. This is done because the gas chromatograph apparatus can not take pressures much greater than atmospheric. A vacuum pump is connected to the pressure bomb, so that the lines and the bomb can be evacuated before taking a sample. When a sample is taken the pressure reduces approximately 30 to 50 kPa in the equilibrium cell, which has negligible affects on the equilibrium. The sample now contained in the pressure bomb is adjusted to attain a reasonable pressure for injection. To achieve the best results, we purge the gas sample through the injection port of the gas chromatograph. After the purging, a sample is then taken at roughly 50 kPa above atmospheric pressure. A sample is taken at equilibrium and at a slightly lower temperature than the equilibrium temperature.

2.1.3 Hydrate Phase Equilibrium Apparatus Modifications to enable gas uptake and Solubility Measurements

The existing apparatus needed to be extensively modified in order to further expand its capabilities of monitoring gas consumption and measuring liquid solubility in the presence of hydrates. These modifications also included the implementation of a data acquisition system as well as software development. All data acquisition programs were written in Visual C++ and are used to monitor pressures, temperature and moles consumed of hydrate forming gas consumed into the bulk liquid phase.

The existing apparatus is shown in figure 2.4. It is equipped with a variable volume reservoir, R, which supplies gas to the reactor in order to maintain the pressure in the reactor constant during a hydrate kinetics experiment, if it is desired to do so.





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The crystallizer and the reservoir are all immersed in an insulated bath consisting of an equal mixture of ethylene glycol and water. A PC is used for direct data acquisition of the experimental pressures and temperatures, and to perform on line calculations of the gas consumption.

In order to obtain a liquid water sample that does not contain any hydrates we must separate the water from the hydrates. For this purpose a micro filter is used (Millipore, Bedford, Massachusetts). The High Pressure filter assembly is able to withstand 3000-psi difference across the filter and separate particles of 25 nm in size, figure 2.5.



Figure 2.5 Simplified Schematic of High Pressure Filter Assembly

A Jefri pump (DBR Engineering, Edmonton, Alberta) was also required to displace the gas volume in the crystallizer to achieve two-phase equilibrium, it is shown in figure 2.6. The Jefri pump is equipped with a 500 cm³ cylinder in order to insert liquid into the pump. The Jefri pump allows the injection of pure water under high pressure into the crystallizer. An Ohaus balance, model number GT410, with \pm -0.001g precision is

used to calculate pure liquid densities and a Ruska Gasometer (Houston, Texas) with two gas chambers, 1000cc and 2000cc, is used to measure the volume of expanded gas to \pm 0.2% of the reading in cm³.



Figure 2.6 Simplified Schematic of Jefri Positive Displacement Pump (DBR Research)

2.1.4 **Procedure for Solubility Experiments**

The hydrate crystallizer is filled with 200 cc of distilled and deionized water. UHP grade CH₄ is supplied from the reservoir via the PID control valve to the hydrate crystallizer until the desired pressure is obtained and maintained throughout the experiment to ensure constant pressure. Once hydrates have formed the procedure for measuring the concentration of dissolved CH₄ in the aqueous phase begins. This procedure is dependent on which region of the phase diagram the experiment is conducted. If the experiment is to be carried out at the three-phase equilibrium (hydrate, gas, liquid water), a sample of the liquid phase is passed through a filter to ensure that all the hydrate crystals have been separated from the aqueous liquid. The sample is then collected in an evacuated pressure bomb which can be removed from the apparatus after it has been filled and has reached mechanical and thermal equilibrium. If the experiment is to be carried out above the three-phase equilibrium line (hydrate and liquid water present), care must then be taken to displace the gas volume with water using the Jefri pump while maintaining constant pressure in the presence of hydrates. The Jefri pump injects water into the crystallizer at a rate at that is sufficient to maintain constant pressure in the crystallizer while gas is being displaced. Water is continuously injected until the gas phase is no longer present. This is necessary in order to obtain two-phase equilibrium between the liquid and solid hydrate phases. After equilibrium has been obtained, between the liquid water and solid hydrate phases, a sample is then taken and passed through the same filter and into an evacuated bomb for analysis.

Subsequently, an analytic flash technique is used to analyze the solubility of the experimental gas in liquid water in the high-pressure bomb. This technique involves the use of the Ruska gasometer, which brings the contents of the bomb at room temperature and pressure into two phases, liquid and gas. The gasometer accomplishes this by allowing the experimental gas to evolve from solution into a graduated piston where the volume of gas can then be measured. The volume of gas required to come out of solution to bring the system to atmospheric pressure is then recorded. The moles of experimental gas in the vapor phase of the gasometer, n_{Exp}^{G} , is computed by

$$n_{Exp}^{G} = \left(P - P_{H2O}^{V}\right) \frac{V}{ZRT}$$

$$(2.1)$$

where P, V, R, T, Z are the atmospheric pressure, volume of the vapor phase in the gasometer, universal gas constant, room temperature, and the compressibility factor for CH₄, respectively. Values for the compressibility factor of the experimental gas were obtained from the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987). $P_{H_{20}}^{\nu}$ is the vapor pressure of water at room temperature which is equivalent to the partial

pressure of water in the gas phase. This now gives us the number of moles of gas that came out of solution in order to satisfy the equilibrium between the experimental gas and water at room temperature and pressure. Since the solubility of experimental gas dissolved in water is known at these conditions, see chapter 3, as well as the volume of water in the bomb, one can calculate the mole fraction of experimental gas, x_{eq} , dissolved in the aqueous phase at the experimental conditions from the following equation.

$$x_{eq} = \frac{\frac{x_g^R n_{H2O}}{1 - x_g^R} + n_{Exp}^G}{\frac{x_g^R n_{H2O}}{1 - x_g^R} + n_{Exp}^G + n_{H2O}}$$
(2.2)

 x_g^R is the mole fraction of experimental gas dissolved in water at room temperature and atmospheric pressure and n_{H2O} is the moles of water in the high-pressure bomb. Since the volume of the high-pressure bomb is known, the mass and number of moles of pure water can then be computed from steam tables at the experimental temperature and pressure (Grigull et al. 1984).

2.1.5 Procedure for Gas Consumption Experiments

In order to measure the amount of gas consumed by the liquid phase the following procedure is used. 150 cc of distilled and deionized water is inserted into the crystallizer under vacuum to ensure that no gas dissolves into the liquid as it is being injected. The reservoir, R1, is charged to a pressure 2000 kPa greater than the experimental pressure in the crystallizer. When the system has achieved thermal and mechanical equilibrium in the crystallizer and reservoir the data acquisition program commences to monitor pressure, temperature and moles consumed. Agitation is then started in the crystallizer and the

pressure is maintained constant in the crystallizer by the control system supplying gas from the reservoir.

2.1.5.1 Procedure for dissolution of methane in water saturated with neohexane

Measurements of the amount of gas dissolved in water saturated with neohexane were performed to see if neohexane facilitates the dissolution of methane gas. A 300 cc beaker was charged with 200 cc of water and 50 cc of neohexane. It was then covered with wax paper and agitated for 30 min. After 30 min the contents of the beaker were allowed to settle and the water was then decanted from the bottom. 150 cc of water saturated with neohexane was then injected into the hydrate crystallizer. The gas phase was flashed 3 times with experimental gas at 500 kPa. Once mechanical and thermal equilibrium was achieved in the crystallizer and reservoir, the data acquisition program was started. Agitation then began in the reactor and the pressure, temperature, and moles consumed were recorded while the reservoir supplied gas to maintain the crystallizer at constant pressure.

2.1.6 Crystal Morphology

The crystal morphology apparatus existed in two forms according to the type of experiment being performed. The experimental apparatus for the morphological studies of structure I hydrate on the methane-water or carbon dioxide-water system is given in the following section. Immediately following is the modification made in order to carry out these studies on the structure H forming system of neohexane-methane-water.

2.1.6.1 Apparatus (Structure I morphology)

The experimental apparatus needed to be modified once again for the purpose of carrying out morphological observations. The stainless steel hydrate crystallizer was modified to have 3 windows, one on the top made from Plexiglas and two on the sides The Lexan windows positioned on the sides of the hydrate made out of Lexan. crystallizer are used for viewing purposes while the Plexiglas window mounted on the top of the reactor is fitted for a fibre optic light pipe which can deliver 40,000 foot-candles of light. The fibre optic light pipe (41720 series, Cole Palmer) is equipped with an infrared filter to eliminate heat transmission. The cooling bath is an equal mixture of filtered water The digital imaging is carried out by a Nikon SMZ 2000 and ethylene glycol. microscope fitted with a 3.34 mega pixel Nikon CoolPix 995 digital camera. The output of the camera is also viewed and recorded by a PC through a Dazzle digital video creator. The droplets are placed on a 316 stainless steel cylinder covered with a layer of Teflon to prevent the water droplets from wetting the surface. Two copper-constantan thermocouples are used to report the temperature in the crystallizer to 0.1 K. One thermocouple is positioned at the surface of the Teflon to measure the surface temperature and one is positioned solely in the gas phase. The pressure in the crystallizer is measured by a Rosemount Smart Pressure transducer (3051CD, Norpac Controls) with a range of 0-13790 kPa and accuracy of 0.075% the span. A simplified schematic is shown in figure 2.7.



Figure 2.7 Experimental Apparatus for Crystal Morphology

2.1.6.2 Apparatus (Structure H morphology)

In the case of Structure H morphological studies, the mass transfer between the methane, neohexane, and water must be aided. Since a water droplet is submerged in a bath of neohexane, one can assume that mutual mass transfer between the two liquid phases is instantaneous at the interface. However, in order to form structure H hydrate the addition of methane gas is required. The methane must dissolve in the neohexane and then travel towards the liquid-liquid interface between water and neohexane. In order to facilitate this step we introduce a stainless steel cylinder open on both ends with a bridge on top to hold a Teflon bar where the water droplet can reside. This stainless steel cylinder allows a Teflon stir bar to be placed inside to agitate the neohexane liquid while minimally disturbing the water droplet.

2.1.7 Crystal Morphology Procedure for Structure I Hydrate

The procedure involves cleaning and removing moisture from the inside of the hydrate crystallizer as well as the stainless steel cylinder and Teflon on which the droplets reside, figure 2.8. The droplets are distilled and dionized water and are placed on the Teflon with the aid of a Hamilton micro syringe. The reactor is then closed and flashed three times with experimental gas at 1000 kPa to remove any residual gas still present in the reactor. The experimental gas, UHP CH_4 or UHP CO_2 , is then fed into the reactor from a reservoir, which is at the experimental temperature.





Extensive trials were conducted in order to choose the best lighting position that would extract the most amount of detail from the crystal formation. It was found that lighting from the back of the reactor made it extremely difficult to view needle formation extending away from the droplets as well as any deviations in the surface sphericity. The lighting assignment that gave the best results was from directly above for structure I experiments.

2.1.8 Crystal Morphology Procedure for Structure H Hydrate

For structure H experiments, the procedure was much the same as structure I except for the lighting arrangement and the presence of the hydrocarbon neohexane. The best lighting arrangement came from the back of the crystallizer in this case. This is because the index of refraction of water and neohexane are very similar and hence light was not being reflected at the surface making it difficult to find the droplet. When lighting was made available from the back the immersed water droplet became visible.

Neohexane was inserted into the crystallizer and immediately following, a water droplet was immersed on a Teflon bar. The Teflon bar was shaped with a concave depression in the middle where the water droplet would reside, see figure 2.9. The contents of the crystallizer were once again flashed three times with experimental gas and when the system was at the experimental temperature and pressure, agitation began.



Figure 2.9 Simplified schematic of the inside of the crystallizer during a Structure H hydrate morphology experiment. (Not to scale)

2.2 LASER LIGHT SCATTERING APPARATUS AT THE UNIVERSITY OF CALGARY

An existing light scatter apparatus existed at the University of Calgary. Kinetic experiments using light scattering techniques were performed on the ethane-water hydrate forming system, which is, known to form structure I hydrate. The experimental apparatus and procedure are given below.

2.2.1 Laser Light Scattering Apparatus and its Modifications

Parent (Parent, 1993, Parent and Bishnoi, 1996) assembled a laser light scattering apparatus at the University of Calgary to perform experiments. He studied the nucleation behaviour of clathrate hydrates using light scattering techniques to characterize the early stages of crystallization. In the following paragraphs the apparatus that Parent used will be described in detail including the modifications that have been made to the apparatus.

The light scattering apparatus that Parent used consisted of a 10mW helium-neon laser (Melles Griot model 05LHP991). The detector is a photomultiplier tube (Oriel model 77348) that is biased by a variable voltage, 0 to -1000 volt range, power supply (Oriel model 70705). The current produced by the photomultiplier, PMT, is amplified to a 0-10 volt signal via a current pre-amplifier (Oriel model 70710) before being processed by the data acquisition computer. The cell, constructed of sapphire and having the following dimensions 3/4" I.D. x 1- 1/4" O.D. x 4-1/2" long, is aligned with the laser and detector with the aid of a custom made optical bench. There are two commercial optical rails (Melles Griot model 07 0RN 001 and 07 0RN 005) secured to a specially designed rotation stage where the sapphire cell rests. The detector rail is attached to a bearing mounted stage that allows the detector 180 degrees of movement about the optical axis. Agitation inside the sapphire cell is achieved with a stir bar that is coupled to a magnetic stirrer on the outside of the reactor. All the light scattering equipment is placed on a vibrational isolation table that absorbs the natural disturbances of the surrounding environment as well as the vibrations caused by the stirring of the contents in the sapphire cell.

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The first modification was to replace the existing cooling system, which used CP grade carbon dioxide with a system based on liquid nitrogen. Liquid nitrogen is much less cost intensive and reduces the time required to reach the experimental temperature. A 35L dewar (Cole-Palmer model 03773-58) that dispenses liquid nitrogen at -190 degrees Celsius was purchased. This liquid nitrogen is then heated to approximately – 150 degrees Celsius with the aid of heating tape. The flow rate is then controlled by a control valve that adjusts the flow rate according to the desired temperature in the sapphire reactor. Finally, stainless steel baffles have also been added to the sapphire cell to avoid the formation of vortices during agitation. Figure 2.10 shows a schematic of the modified light scattering apparatus.

The previous light scattering setup could not maintain a constant experimental pressure, therefore the apparatus was modified accordingly. This involved attaching the existing gas feed line to a supply reservoir, R1. The supply reservoir is then able to deliver gas to the sapphire equilibrium cell, in order to maintain a constant pressure. A data acquisition program for the light scattering apparatus was written and installed in order to monitor the experimental temperature and pressure. The program also records the voltage from the photomultiplier, which could later be used to calculate the hydrodynamic particle growth.



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2.2.2 Laser Light Scattering Procedure

In order to measure the rate of hydrate growth on latex spheres the following procedure is followed. Reservoir, R1, is filled to approximately four bars above the target experimental pressure. R1 is the supply reservoir which delivers gas to the sapphire cell reactor in order to maintain a constant pressure throughout the growth experiment and hence a constant driving force for nucleation and growth. The bias reservoir, R2, is then filled to approximately half a bar below the experimental pressure. This is to ensure the accurate measurement of the pressure in the supply reservoir, R1. The reactor is then charged with water and a known amount of monodispersed latex particles. The cell is flashed 3 times with experimental gas at 1000 kPa and then pressurized to the experimental pressure.

kept constant by flowing nitrogen through the annular region around the sapphire cell reactor. The laser is then focused near the gas-liquid interface because this is where nucleation will initially begin due to the higher concentration of dissolved gas at the interface. The photomultiplier is fixed in place perpendicular to the incident light from the helium neon laser. The laser is then turned on and the data acquisition program commences to log the photomultiplier voltage, pressure and temperature during the experiment. It should be noted that the validation of this technique was not dependent on the hydrate forming gas and hence ethane-water was selected as the model system out of convenience.

Chapter 3

SOLUBIILITY MEASUREMENTS IN THE HYDRATE FORMATION REGION

The amount of methane and carbon dioxide dissolved in pure water in the presence of its corresponding gas hydrate has been measured. Experiments for the carbon dioxide-water system were performed at temperatures between 273-284 K and pressures ranging form 20-60 bar. Experiments for the methane-water system was carried out at temperatures between 274-285 K and pressures ranging form 35-65 bar.

3.1 SOLUBILITY OF CARBON DIOXIDE

Solubility experiments were conducted at the three-phase equilibrium and in the hydrate formation region. Experimental conditions ranged from 273-284 K and 20-60 bar. The measurements are given in table 3.1 and are also plotted in figure 3.1. The experimental uncertainties range from 3-5% and are calculated using a procedure given in Appendix A. As seen in table 3.1, six measurements of the solubility of CO_2 in water were made at pressures below the three-phase equilibrium to illustrate the known trend in the absence of hydrate. In the absence of hydrate, the solubility of CO_2 in water increases with decreasing temperature.

Table 3.1 Mole fraction of CO2 ir	water at given pressures	and temperatures (Servio and
Englezos, 2001)		

Temperature (K)	Pressure (bar)	X _{eq}	Phases Present
277.05	20	0.0181	H-Lw-V
275.95	20	0.0173	H-Lw
273.95	20	0.0164	H-Lw
277.05	37	0.0196	H-Lw
274.15	37	0.0158	H-Lw
281.65	37	0.0245	H-Lw-V
278.15	42	0.0198	H-Lw
274.05	42	0.0156	H-Lw
282.55	42	0.0256	H-Lw-V
274.05	50	0.0163	H-Lw
278.05	50	0.0198	H-Lw
282.85	50	0.0275	H-Lw
274.25	60	0.0163	H-Lw
276.45	60	0.0192	H-Lw
282.95	60	0.0281	H-Lw
278.05	20	0.0183	Lw-V
280.45	20	0.0170	Lw-V
282.25	20	0.0156	Lw-V
281.55	30	0.0222	Lw-V
283.05	30	0.0210	Lw-V
283.15	37	0.0234	Lw-V

H, Lw, and V are the solid hydrate, liquid water, and vapor, respectively



Figure 3.1 Mole Fraction of CO₂ dissolved in Water (Servio and Englezos, 2001)

Our results for the solubility of CO_2 in water in the presence of hydrates clearly show that at a given pressure the solubility of gas dissolved in liquid decreases with decreasing temperature in the hydrate formation region. This conclusion is in agreement with the experimental results of (Yang et al., 2000; Yamane and Aya, 1995; Kimuro et al., 1994) as well as the conclusions of Ohmura and Mori (1999). It can also be seen that the solubility is not a strong function of pressure over the hydrate formation region. This can also be shown by comparing the results of Yang et al. with this work for selected temperatures and pressures, table 3.2.

Fable 3.2	Solubility of CO ₂ in water at selected temperatures and pressures to illustrate
	the negligible effect of pressure on the solubility in the presence of gas.
	hydrate (Servio and Englezos, 2001).

Temperature (K)	Pressure (bar)	x_{eq} (mole fraction)
273.95	20	0.0164
274.25	50	0.0163
278.05	50	0.0198
278.37	103.5	0.0227*
280.34	142	0.0260*
280.98	61	0.0269*

* values from Yang et al. (2000)

The results from this work were also used to validate the assumption made by Englezos et al. (1987). Englezos et al. assumed that x_{eq} , the solubility of gas dissolved in liquid in equilibrium with gas hydrates, was given by the following relation

$$x_{eq} = \frac{f(P_{eq}, T_{exp})}{H}$$
(3.1)

in the hydrate formation region. f is the fugacity of the pure gas at the experimental temperature, T_{exp} , and at the three-phase equilibrium pressure, P_{eq} , not the experimental pressure, P_{exp} , and H is simply Henry's constant. The fugacity of the gas at the experimental temperature and three-phase pressure was computed using the Trebble-Bishnoi (1987) equation of state and Henry's law constants were given by Malegaonkar et al. (1997) and Carroll et al. (1991) for CO₂. The Poynting correction factor was used for both Carroll and Malegaonkar 's Henry's constants at elevated pressures. As one can see from table 3.3, our experimental results are in very good agreement with Englezos predictions.

Table 3.3Percentage difference between this works experimental determined
solubility (mole fraction of CO_2 in water) and those calculated using
Englezos et al. assumption (Servio and Englezos, 2001).

T (K)	P (bar)	x _{eq}	x _{eq} predicted*	x _{eq} predicted**	$100 \frac{(x_{eq} * - x_{eq})}{x_{eq} *}$	$100 \frac{(x_{eq}^{**} - x_{eq})}{x_{eq}^{**}}$
277.05	20	0.0181	0.0196	0.0197	7.7	8.1
275.95	20	0.0173	0.0178	0.0178	2.8	2.8
273.95	20	0.0164	0.0157	0.0156	-4.5	-5.1
277.05	37	0.0196	0.0196	0.0197	0.0	0.5
274.15	37	0.0158	0.0160	0.0158	1.2	0.0
281.65	37	0.0245	0.0262	N/A	6.5	N/A
278.15	42	0.0198	0.0207	0.0209	4.3	5.3
274.05	42	0.0156	0.0162	0.0160	3.7	2.5
282.55	42	0.0256	0.0270	N/A	5.2	N/A

* Using Carroll's correlation for Henry's Constants

** Using Malekognar's experimentally determined Henry's Constants

The percentage difference between the calculated and experimentally determined solubility is never more than 8.1 percent. Thus, the assumption made by Englezos et al. in the hydrate kinetics model is valid. The comparison between values was not done at pressures above 42 bar. Above this pressure CO_2 is a liquid and Henry's constants are not available. The liquid CO_2 equilibrium points are also outside the region to validate the kinetics assumption.

3.2 SOLUBILITY OF METHANE

Experiments were conducted at the three-phase equilibrium and in the hydrate formation region. The conditions ranged from 274-285 K and 35-65 bar. The measurements are given in table 3.4 and are also plotted in figure 3.2. The experimental uncertainties range from 5-9% and are calculated using a procedure given in Appendix A

As seen in table 3.4, six measurements of the solubility of CH_4 in water were made below the three-phase equilibrium to illustrate the known trend in the absence of hydrate. In the absence of hydrate, the solubility of CH_4 in water increases with decreasing temperature.

Temperature (K)	Pressure (bar)	x _{eq} (mole fraction)	Phases Present
274.35	35	0.001170	H-Lw
275.45	35	0.001203	H-Lw
276.25	35	0.001240	H-Lw-V
278.65	35	0.001190	Lw-V
280.45	35	0.001102	Lw-V
274.15	50	0.001190	H-Lw
277.35	50	0.001360	H-Lw
279.65	50	0.001600	H-Lw-V
281.55	50	0.001524	Lw-V
282.65	50	0.001357	Lw-V
275.25	65	0.001201	H-Lw
280.15	65	0.001567	H-Lw
282.05	65	0.001850	H-Lw-V
283.25	65	0.001720	Lw-V
284.35	65	0.001681	Lw-V

Table 3.4 Mole fraction of CH₄ in water at given pressures and temperatures (Servio and Englezos, 2002)

H, Lw, and V are the solid hydrate, liquid water, and vapor, respectively

Our results for the solubility of CH_4 in water in the presence of hydrates clearly show that at a given pressure the solubility of gas dissolved in liquid decreases with decreasing temperature in the hydrate formation region. This conclusion is in agreement with the theoretical calculations (Zatsepina and Buffett, 1997) as well as the conclusions of Ohmura and Mori (1999). It can also be seen that the solubility is not a strong function of pressure over the hydrate formation region.


Figure 3.2 Mole fraction of Methane in Water (Servio and Englezos, 2002)

The results from this work were once again used to validate the assumption made by Englezos et al. (1987). The fugacity of the gas at the experimental temperature and three-phase pressure was computed using the Trebble-Bishnoi (Trebble and Bishnoi, 1987) equation of state and Henry's law constants were given by Lekvam and Bishnoi (1997) and Carroll and Mather (1997) for CH_4 . The Poynting correction factor was used for both Lekvam and Bishnoi (1997) and Carroll and Mather (1997) Henry's constants at elevated pressures. The results were compared with the measurements obtained in this work. As one can see from table 3.5, our experimental results are in very good agreement with the predictions by Englezos et al. (1987). The percent difference between the results is never more the 9.3 percent.

Table 3.5	Percentage difference between this works experimental determined solubility
	(mole fraction of CH ₄ in water) and those calculated using Englezos et al.
	(1987) assumption (Servio and Englezos, 2002)

T (K)	P (bar)	X _{eq}	x _{eq} predicted*	x _{eq} predicted**	$100 \frac{(x_{eq} * - x_{eq})}{x_{eq} *}$	$100 \frac{(x_{eq} * * - x_{eq})}{x_{eq} * *}$
274.35	35	0.00117	0.00113	0.00114	-3.8	-2.7
275.45	35	0.00120	0.00117	0.00118	-2.5	-2.0
276.25	35	0.00124	0.00122	0.00122	-1.8	-1.6
274.15	50	0.00119	0.00112	0.00113	-6.1	-4.9
277.35	50	0.00136	0.00129	0.00129	-5.1	-5.4
279.65	50	0.00160	0.00149	0.00147	-7.4	-8.6
275.25	65	0.00120	0.00116	0.00117	-3.2	-2.6
280.15	65	0.00157	0.00154	0.00152	-1.9	-3.3
282.05	65	0.00185	0.00172	0.00169	-7.4	-9.3

* Using Carroll's correlation for Henry's Constants

** Using Bishnoi's interpolated Henry's Constants

3.3 THEORETICAL ASPECTS

At constant pressure the following relation may express the change in solubility with temperature (Prausnitz et al., 1986):

$$\left(\frac{d\ln(x)}{d\left(\frac{1}{T}\right)}\right)_{P} = -\frac{\Delta \overline{h}}{R}$$
(3.2)

where $\Delta \overline{h}$ is a function of the partial molar enthalpy as follows:

$$\Delta \overline{h} = -(h^G - h^L) + (\overline{h}^L - h^L)$$
(3.3)

 h^{L} and h^{G} denote the enthalpy of the solute in the hypothetical pure liquid and gas states. \overline{h}^{L} is the partial molar enthalpy. The first term in equation 3.3 is simply the enthalpy of vaporization while the second term give the partial molar enthalpy of mixing. Investigating equation 3.3 tells us that if the enthalpy of vaporization is greater than the partial molar enthalpy of mixing, the solubility falls with increasing temperature. This is true for the solubility of methane and carbon dioxide in water below the hydrate formation pressure at a given temperature. If the partial molar enthalpy of mixing dominates, $\Delta \overline{h}$ becomes positive and the solubility rises with increasing temperature. The partial molar enthalpy of mixing becomes large when the cohesive energy density between solute and solvent becomes great. This is the case for the solubility of carbon dioxide and methane in the presence of hydrates.

3.4 CONCLUSIONS

The solubility of CO_2 and CH_4 dissolved in liquid water and in the presence of gas hydrate was measured at temperatures varying from 274 K to 285 K. Pressures range from 20 bar to 65 bar. Results show that solubility decreases with decreasing temperature in the hydrate formation region. In addition the solubility is not a strong function of pressure over the hydrate formation region. Finally, the results are in agreement with the theoretically calculated values using an equation of state and Henry's law. It is important to note that the deviation between experimental and theoretical solubility is always positive for carbon dioxide except for one case and always negative for methane. This may indicate the need to for an adjustable parameter in the theoretical approach to account for different gas-water interactions on the molecular level.

Chapter 4

CH₄-CO₂-NEOHEXANE PHASE EQUILIBRIA IN THE HYDRATE REGION

Incipient equilibrium hydrate formation conditions for the methane-carbon dioxide-neohexane-water system were obtained by employing the isothermal pressure search method. Two gas mixtures comprised of 80% methane 20% carbon dioxide and 50% methane 50 % carbon dioxide on a water-free basis were used.

4.1 PHASE EQUILIBRIA DATA

Experiments at NRC showed that carbon dioxide with neohexane and ice forms structure H hydrate (Ripmeester, 1992). Our objective was to check whether structure H hydrate could form from liquid water. Liquid water was chosen because liquid water is the most common form of water in oil reservoirs and oceans. In spite of efforts to nucleate such hydrate in liquid water, it was not possible to obtain hydrates of structure H. The hydrate that was formed was stable within the carbon dioxide structure I hydrate equilibrium conditions. Two gas mixtures were used. The first had a 50-50 % molar concentration of methane and carbon dioxide. All the measurements are shown in Tables 4.1 and 4.2.

T (K)	P (MPa)	CH ₄ mole fraction	CO ₂ mole fraction
273.45 ^(b)	1.780	0.4653	0.5347
274.0 ^(a)	2.300	0.8216	0.1784
274.2 ^(b)	1.830	0.4660	0.5340
275.2 ^(b)	2.050	0.4697	0.5303
275.6 ^(b)	2.120	0.4701	0.5299
275.7 ^(b)	2.200	0.4729	0.5271
276.0 ^(a)	2.600	0.8421	0.1579
276.8 ^(b)	2.400	0.4801	0.5199
277.1 ^(a)	3.000	0.8575	0.1425
278.3 ^(a)	3.400	0.8756	0.1244
278.4 ^(b)	2.825	0.4861	0.5139
278.7 ^(b)	2.851	0.496	0.504
279.5 ^(b)	3.301	0.5002	0.4998
279.7 ^(b)	3.351	Not Measured	Not Measured
280.1 ^(b)	3.370	0.5040	0.4960
281.8 ^(b)	4.410	0.5042	0.4958
283.0 ^(b)	5.001	0.5058	0.4942
283.1 ^(b)	5.070	0.5162	0.4838

Table 4.1 Incipient equilibrium hydrate formation conditions data and gas phase molar composition for the methane-carbon dioxide-water system

(a) The gas mixture is 80 % methane and 20 % carbon dioxide on a molar basis (b) The gas mixture is 50 % methane and 50 % carbon dioxide on a molar basis

Table 4.2	Incipient e	quilibrium	hydrate formation co	onditions data and gas	s phase m	ıolar
	composition	n for the n	nethane-carbon diox	ide-neohexane-water	system.	The
	superscripts	s(a) and (b)	nave the same mean	ing as in Table 4.1.		
	T(V)	$D(MD_{\alpha})$	CII male fraction	CO male fraction		

		CT14 mole machon	CO_2 mole mattion
273.9 ^(b)	1.310	0.4331	0.5669
274.3 ^(b)	1.380	0.4371	0.5629
274.6 ^(a)	1.300	0.7430	0.2570
275.1 ^(b)	1.540	0.4410	0.5590
275.4 ^(b)	1.610	0.4454	0.5546
275.5 ^(b)	1.700	0.4461	0.5539
275.6 ^(b)	1.750	0.4465	0.5535
275.6 ^(a)	1.500	0.7496	0.2504
275.9 ^(b)	1.810	0.4511	0.5489
276.1 ^(b)	1.840	0.4529	0.5471
276.1 ^(b)	1.850	Not Measured	Not Measured
276.9 ^(b)	2.180	0.4593	0.5407
277.4 ^(b)	2.461	Not Measured	Not Measured
277.5 ^(a)	1.850	0.7631	0.2369
277.7 ^(b)	2.500	0.4662	0.5338
278.8 ^(b)	3.001	Not Measured	Not Measured
279.1 ^(a)	2.250	0.7737	0.2263
279.7 ^(b)	3.351	Not Measured	Not Measured
280.6 ^(a)	2.750	0.7778	0.2222
280.6 ^(b)	3.500	0.4960	0.5040
281.2 ^(b)	4.000	0.5226	0.4774
281.6 ^(a)	3.000	0.7814	0.2186
282.9 ^(a)	3.600	0.7840	0.2160
283.2 ^(b)	5.100	0.5421	0.4579

Chapter 4: CH₄-CO₂-Neohexane Phase Equilibria in the hydrate region

Figure 4.1 shows the hydrate equilibrium measurements for the 80-20 mixture in pure water and in a neohexane containing system. As seen from the plot when neohexane is present hydrates form at pressures lower by about 10 bar. This difference is not merely caused by the presence of neohexane. If neohexane does not participate in the crystal structure then its presence would only affect the structure I hydrate formation conditions. This effect, however, is not expected to cause a depression of the hydrate formation conditions by 1 MPa. In our opinion, the results indicate that structure H hydrate is formed. A definite conclusion would have been possible if the solid phase could be isolated and then analyzed. Such an experiment, however, has a number of difficulties and is beyond the current state-of-the-art in hydrate research.

Figure 4.2 shows the results for the 50-50 % mixture. As seen from the graph, at temperatures greater than approximately 277.5 K the hydrate formation conditions in the presence of neohexane are in the vicinity of those in pure water. In our opinion, structure I hydrate forms above 277.5 K. Below that temperature, however, the incipient hydrate formation conditions start diverging. It is reasonable to assume that structure H begins to form. It is also possible that a mixture of structure H and structure I hydrate exists. In other words a solid structure breaks down into two solids in a similar fashion that a stable liquid phase undergoes a liquid-liquid phase separation. Verification of Structural transition may be performed by NMR (Ripmeester et al., 1987; 1990; 2000; Konstantin and Ripmeester, 1999) and Raman Spectroscopy (Sloan et al., 1998b; Subramanian et al., 2000; Tulk et al., 2000). Such experiments are beyond the scope of this work.



Figure 4.1 Incipient gas hydrate formation conditions from a gas mixture containing 80mole % methane and 20-mole % carbon dioxide, water and neohexane (Servio et al., 1999).



Figure 4.2 Incipient gas hydrate formation conditions from a gas mixture containing 50mole % methane and 50-mole % carbon dioxide, water and neohexane (Servio et al., 1999).

4.2 CONCLUSIONS

Equilibrium hydrate formation experiments with a 80-20 % and a 50-50 % methane- carbon dioxide mixture together with neohexane were performed and the incipient hydrate formations were determined. It appears that the 80-20 gas mixture forms structure H hydrate. The results from the 50-50 mixture indicate that above a temperature of approximately 277.5 K structure I crystals are formed. Below that temperature, however, a transition might occur resulting in structure H or a mixture of structure H and I hydrate.

Chapter 5

ETHANE HYDRATE GROWTH EXPERIMENTS IN THE PRESENCE OF LATEX PARTICLES

Knowledge of the intrinsic kinetics of methane and carbon dioxide hydrate formation is required in order to model such applications as the formation of carbon dioxide hydrates in the ocean or formation of methane hydrate in the earth. Hydrate nuclei are extremely small and current laser light scattering techniques are not able to successfully detect or measure the size of these nuclei and hence, the growth rate starting from nuclei. Ethane hydrate growth experiments were performed in this study on two substrates of known initial size, in particular on latex particles of known diameter and charge.

5.1 LASER LIGHT SCATTERING EXPERIMENTS

Five experiments were performed on the ethane-water system; two with positively charged latex particles, two with negatively charged latex particles, and one without latex particles. The experimental conditions along with the nucleation times for each experiment are presented in table 5.1. The experiments given in table 5.1 were not repeated. It is noted that the induction time measurement was based on photomultiplier response as well as visual observation. The values of the induction times are compared to those predicted by the following correlation from Natarajan et al. (1994).

$$t_{ind} = K \left(\frac{f_g^{\nu}}{f_{eq}} - 1 \right)^{-m}$$
(5.1)

where K and m are fitted parameters depending on the hydrate forming gas. The value of K and m for ethane are 42.85 seconds and 1.38, respectively. f_g^v is the fugacity of the gas at the experimental temperature and pressure and f_{eq} is the fugacity of the gas at the three-phase equilibrium. The fugacity of the vapor phase is calculated using the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987)

The observed values of the induction time do not agree well with the predicted values. This could be due to the fact that adequate agitation could not be achieved in the sapphire tube reactor. Natarajan and Bishnoi's correlation was developed to model induction time in a well-mixed reactor which would give rise to smaller induction times.

For each experiment the photomultiplier voltage was logged vs. time. The results for the five experiments are all very similar therefore only the results of experiments 1,2, and 4 are given and can be seen in figures 5.1, 5.2, and 5.3.

Exp	T (K)	P (kPa)	Particle Charge	Particle Size (nm)	Particle number per milliliter	Induction Time predicted (min)	Induction Time observed (min)
1	278.3	1300				3	130
2	278.3	1300	Positive	600	1.92E+8	3	154
3	278.1	1300	Positive	600	3.84E+8	3	167
4	278.5	1300	Negative	692	2.69E+8	3	94
5	278.2	1500	Negative	692	2.69E+8	2	85

Table 5.1 Experimental Conditions and Induction Times (Servio et al., 2000)

Note: At 278.8 K the ethane hydrate equilibrium pressure is 950 kPa (Sloan, 1998)

In figure 5.1 the photomultiplier voltage vs. time for a hydrate formation experiment in the absence of latex particles is plotted. The figure shows a baseline photomultiplier voltage of 0.11 volts. The voltage remains constant until hydrate nucleation, approximately 7800 seconds after the experiment was started, where the voltage begins to increase rapidly. It should be noted that the rapid increase in voltage coincided with the visually observed turbidity point in all five experiments performed.

Figure 5.2 shows the photomultiplier voltage vs. time for a hydrate formation experiment in the presence of positively charged latex particles. The baseline voltage is now slightly higher than in figure 5.1 due to the presence of the latex particles, and is approximately equal to 0.14 volts. Once again the voltage remains constant until hydrate nucleation, approximately 9000 seconds after the experiment began. The voltage then begins to increase in the same manner as in figure 5.1.







Figure 5.2 PMT Response Vs Time (Positively Charged Particles) (Servio et al., 2000)





The photomultiplier voltage vs. time for a hydrate formation experiment in the presence of negatively charged latex particles is shown in figure 5.3. The baseline voltage for this experiment is approximately 0.17 volts, which is higher than the baseline voltage in figures 5.1 and 5.2 because of the higher concentration of latex particles. The voltage is constant until hydrates appear, 5600 seconds into the experiment. The voltage then increases with approximately the same rate as that of figures 5.1 and 5.2.

A comparison of figures 5.1, 5.2, and 5.3 indicates a need to perform more experiments in order to distinguish between the hydrate nucleation and growth behavior in the absence and presence of latex particles. In order to further this research, modifications must be performed on the current light scattering apparatus.

The intensity of scattered light that is measured by the photomultiplier is dependent on the following:

- 1) Index of refraction of the latex particles, hydrates, and water.
- 2) The wavelength of the laser.
- 3) Concentration of particles.
- 4) Particle size distribution.
- 5) Agitation of Particles.

The index of refraction of latex and water can be readily found in any physics book and methods for calculating the index of refraction of gas hydrates using a modified Lorenz-Lorentz model is given by Herri et al. (Herri and Gruy, 1995). Values of the refractive indexes of water, polystyrene (latex), and methane hydrate (structure I) are given in table 5.2.

	Water (589 nm, 20 ⁰ C) (Halliday et al.,1993)		Polystyrene (590 nm, 20 ⁰ C) (Interfacial Dynamics Corp.)	Methane Hydrate (750 nm, 1 ⁰ C) (Herri and Gruy, 1995)	
Index of Refraction		1.33	1.591	1.346	
	-		Helium-Neon Laser at UofC	_	
		Wavelength	634 nm		

Fable 5.2 .	Indices of	Refracti	ion and La	iser Wavel	length
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The wavelength of a laser is dependent on the type of light source used and is known prior to the experiment, see table 5.2. Now in order to experimentally determine the particle size distribution and the concentration of particles, the method of photon correlation spectroscopy (Cummins and Pusey, 1977; Berne and Pecora, 1976) must be implemented. Photo correlation spectroscopy requires either a real time autocorrelator or a spectrum analyzer (Mcquarrie, 1976) which are very costly and outside the project budget. Cost estimates were obtained from Malvern Instruments for a real time autocorrelator. Values given were approximately \$30,000 USD, with accompanying computer and software necessary for the operation of the autocorrelator. Without this equipment it is not possible to differentiate between the effects of the particle size distribution, the particle concentration, and the agitation of the hydrate slurry on the intensity of scattered light. It can then be concluded that the apparatus as it exists at the University of Calgary can only be used to determine the onset of hydrate nucleation.

Another limitation of this project was the formation of a hydrate layer at the gasliquid interface, which was observed in all the experiments performed. The hydrate layer occurred approximately 200s after hydrate nucleation. The presence of a hydrate layer hinders the diffusion of gas into the liquid phase and as a result impedes hydrate growth.

Chapter 5: Ethane Hydrate Growth Experiments In the presence of Latex Particles

The following steps were taken in order to achieve better agitation in the liquid phase: (a) addition of baffles (b) increase in stir bar rpm. The addition of baffles as well as increasing the stirrer speed had no affect in eliminating the formation of a hydrate layer at the gas-liquid interface. It is believed that the gas-liquid surface area is not large enough to allow sufficient mass transfer of the gas into the liquid bulk. The only solution is therefore to increase the diameter of the reactor and further modify the light scattering apparatus. The current light scattering setup is unable to monitor particle sizes and particle size distribution without the aid of a real time autocorrelator or spectrum analyzer. Since it was not feasible to purchase the above equipment, it was therefore not practical to modify the sapphire cell reactor in order to increase the gas-liquid surface area.

5.2 CONCLUSIONS

Experiments have been performed on the ethane-water system in the presence of positively and negatively charged latex particles, each having a diameter of 600 nm and 692 nm respectively. The experiments were carried out at temperatures between 278.0 K and 278.6 K with pressures ranging from 1300 kPa to 1500 kPa. More work needs to be performed with additions to the existing apparatus in order to differentiate between the hydrate nucleation and growth behavior with and without latex particles.

Chapter 6

A MORPHOLOGY STUDY OF STRUCTURE I GAS HYDRATES

Morphological studies on the formation of methane or carbon dioxide hydrate crystals on nearly spherical water droplets have been performed. Each experiment was performed with two droplets approximately 5 mm and 2.5 mm in diameter or three droplets with a diameter of approximately 2.5 mm. The experimental temperature was arbitrarily set at 274.65 K. Two experimental pressures, 2150 kPa and 1000 kPa above the three-phase hydrate equilibrium pressure at the experimental temperature were chosen in order to monitor the effects of driving force on the crystal morphology

6.1 CRYSTAL MORPHOLOGY

Crystal Morphology experiments have been carried out on water droplets immersed in either a methane or carbon dioxide gas atmosphere. Experimental work was performed at 274.65 K and under two different pressures to observe the effect of driving force. The two experimental pressures were 2150 kPa, high driving force, and 1000 kPa, low driving force, above the three-phase equilibrium for methane and carbon dioxide. The three-phase equilibrium conditions for carbon dioxide and methane hydrate are 1386 kPa at 274.4 K and 2900 kPa at 274.3 K, respectively (Sloan, 1998a).

The induction times for the nucleation of hydrates on water droplets can be estimated as a function of supersaturation by using the following correlation by Natarajan et al. (1994):

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$$t_{ind} = K \left(\frac{f_g^{\nu}}{f_{eq}} - 1\right)^{-m} \tag{6.1}$$

where K and m are fitted parameters depending on the hydrate forming gas. The value of K and m for CO₂ are 189.56 seconds and 0.91, respectively. The values of K and m for CH₄ are 311.64 seconds and 1.21, respectively. f_g^v is the fugacity of the gas at the experimental temperature and pressure and f_{eq} is the fugacity of the gas at the threephase equilibrium. The fugacity of the vapor phase is calculated using the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987)

The first set of experiments were performed under high driving force. Table 1 gives the experimental conditions for both high and low driving force experiments along with their corresponding nucleation times. In each of these experiments, three water droplets approximately 2.5 mm in diameter were present. It was observed that the nucleation time for all three droplets was within fractions of a second of each other. In other words it was found that for each experiment all water droplets present in the system would nucleate simultaneously. From table 6.1 hydrate nucleation on water droplets for both systems under high driving force fell within 10-90 min. These values were between 4.5 to 9.4 times larger than those predicted using the correlation by Natarajan et al.. This is probably due the fact that the interface was stagnant and not mixed therefore causing higher mass transfer resistance. The correlation by Natarajan et al. was given for bulk water in an agitated vessel.

Within a few seconds (less then 5 seconds) after nucleation the surface of the water droplet quickly became jagged and exhibited many fine needle like crystals extruding away for the gas-hydrate-water interface as seen in figure 6.1. This was true for

all cases observed under high driving force, independent of hydrate forming gas. It can also be seen from figure 6.1 that the thickness and length of the hydrate needles extruding

# Droplets	Gas	Size (mm)	P (kPa)	t _{predicted} (min)	t _{measured} (min)
3	CO ₂	2.5	3540	3	13
3	CO ₂	2.5	3540	3	24
3	CO_2	2.5	3540	3	17
3	CH ₄	2.5	5100	9	85
3	CH ₄	2.5	5100	9	79
3	CH ₄	2.5	5100	9	37
2	CO_2	5 & 2.5	3540	3	. 39
2	$\rm CO_2$	5 & 2.5	3540	3	14
2	CO_2	5 & 2.5	3540	3	21
2	CO_2	5 & 2.5	2390	5	*
2	CO_2	5 & 2.5	2390	5	478
2	CO_2	5 & 2.5	2390	5	562
2	CH ₄	5 & 2.5	5100	9	60
2	CH_4	5 & 2.5	5100	9	44
2	CH_4	5 & 2.5	5100	9	29
2	CH ₄	5 & 2.5	3950	22	*
2	CH_4	5 & 2.5	3950	22	587
2	CH_4	5 & 2.5	3950	22	*

Table 6.1 List of experimental conditions along with predicted and measured induction times.

* Did not nucleate within 5 days

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Figure 6.1 Methane hydrate covering the surface of a water droplets (a,b,c) under high driving force, 10 minutes after nucleation. Picture (d) is a magnified view of droplet (c).

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from the surface affect the size of the droplet. Droplet 6.1c was initially of the same size of droplets 6.1a and 6.1b. It decreased in size significantly with respect to the first two droplets because of the amount of water that participated in forming the elaborate network of crystals extending away for the hydrate-gas interface.

The next sets of experiments were performed in order to gain a better understanding of the effect of driving force and droplet size on the macroscopic crystal morphology. Two water droplets of approximately 5 and 2.5 mm were positioned in the hydrate crystallizer. It was observed that the nucleation times once again fell in the same range as the previous experiment, under high driving force, and that the droplets both nucleated at approximately the same time. Therefore, the droplet size has no effect on the induction time for hydrate nucleation. There were three apparent phases that took place when hydrate crystals formed on the water droplets. The first phase was the appearance of a hydrate layer around the water droplet along with the needle like crystals as seen in figure 6.2. After a period of time, up to 10 hours after the onset of nucleation, the needlelike crystals grew in size and thickness. The second phase started with the collapse of most of the crystals needles onto the hydrate layer covering the water droplet. The last phase was the appearance of depressions in the hydrate layer surrounding the water droplet. It should be noted that the appearance of the third phase could take from 10 to 15 hours to a couple of days is some cases. The collapse of the hydrate layer surrounding the water droplets gives proof that water is still being consumed from within the droplet for hydrate formation. In other words, the hydrate layer does not prevent hydrate formation.

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(a) Time 1hour



2 mm

(b) Time 5 hours



(c) Time 20 hours

Figure 6.2 Carbon dioxide hydrates covering two water droplets under high driving force at three different times.

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Low driving force conditions presented a problem in the sense that half of the experiments performed had to be terminated due to the lack of hydrate activity. If no hydrate crystals formed within 5 days, the experiment was terminated. One experiment for methane and two for carbon dioxide formed hydrates under low driving force as seen in table 6.1. Once again our measured inductions times exceeded those calculated using the correlation by Natarajan and Bishnoi by up to 108-fold. When the hydrates formed under low driving force the first observation was the absence of any hydrate needles from the hydrate-covered droplet. The texture was smooth and shiny and is shown in figure 6.3. Once again, after approximately 10 hours, signs of the hydrate layer collapsing inward were visible and eventually the hydrate layer collapsed appreciably. This is once again proof of continuous hydrate growth after the surface of the water droplets are covered with a hydrate layer. Figure 6.4 shows a comparison in the surface morphology between high driving force and low driving force conditions. The droplets created under low driving force are smooth and shinny, while the high driving force droplets are rough and dull.

The difference in surface roughness and the appearance of hydrate needles can be postulated to depend on the density of hydrate nuclei formed which in turn depends on the magnitude of the driving force. Under high driving force nucleation occurs at a larger number of sites on the droplet surface compared to the number of sites under low driving force. According to homogenous crystallization theory, the rate of nucleation (amount of nuclei formed per unit time per unit volume) increases with the degree of supersaturation (Mullin, 1997). The degree of supersaturation is proportional to the driving force. Subsequently, growth takes place preferentially at these sites because it is energetically favourable.

The actual mechanism of hydrate growth on the water droplets is not known but we may assume that water is being drawn up the hydrate through capillary action through the porous hydrate layer and "reacts" with gas that is widely available. Higher driving forces give rise to many crystal growth centers with kinetics greater than at lower driving forces. It can be postulated that the higher kinetics gives rise to more random crystal growth leading to rough surfaces. In low driving force conditions, nucleation occurs at a decreased number of sites, compared to higher driving force. Due to the decreased density of nucleation sites, more free water on the surface of the droplet is available for the growth of nuclei. The kinetics are also slower which gives more uniform crystal growth. Hence, growth occurs across the surface of the droplet until the entire droplet is covered in a smooth layer of hydrate. After the surface has been covered growth probably occurs via water permeating through the hydrate layer into the gas-hydrate interface where it once again "reacts" with an abundance of gas. One also should keep in mind that gas may diffuse through the hydrate layer and "react" with free water (Hatzikiriakos and Englezos, 1994). The relative magnitude of these two phenomena is difficult to establish.

It is interesting to note that Ohmura et al. (1999) also observed the appearance of crystals growing radially around their hydrate covered surface. They described these crystals as plate-like and standing upright on the outer surface of the drop-enclosing hydrate shell formed. They also noted that the plate like crystals was never observed in the presence of pure water and/or small subcooling (~ 2 K). This result is consistent with



nours



Figure 6.3 Methane hydrates covering two water droplets under low driving force at three different times.



(a) Time 25 hours



(b) Time 25 hours

1 mm

Figure 6.4 Comparison of methane hydrate surfaces from water droplets under low, (a), and high, (b), driving forces.

Chapter 6: A Morphology Study of Structure I Gas Hydrates

our findings of needle like crystals extruding radially from the surface of our hydratecovered droplets under high driving force. It was observed in all morphologically formation experiments immediately after nucleation hydrates covered the entire surface of the droplet within a second in a manner that resembles later growth coverage. Hydrates appeared on a random side of the water droplet and then laterally grew to cover the entire surface.

Finally, experiments were performed to observe the decomposition of hydrates on the water droplets. These experiments were carried out at a pressure 10% below the three-phase equilibrium pressure. Decomposition of the hydrates was macroscopically the same for high and low driving force and independent of the hydrate forming gas. All hydrates disappeared from macroscopic view approximately 30 minutes after the pressure decrease. Figure 6.5 shows two water droplets covered by hydrates as they decomposed. It is noted that this figure is a continuation of figure 6.2. The hydrate surface looks almost liquid like or gel like after 5 minutes of dissociation and quickly begins to smooth out. Minutes later the gas-liquid surface was visible as well as hydrate sheets within the droplets. These hydrate sheets as seen in figure 6.6 were thin and transparent and migrated to the top of each droplet until they vanished completely. Droplets of gas inside the water droplets were also seen rising to the top with the hydrate sheets and can be seen in figure 6.6.



(a) Time 5 mins



(b) Time 20 mins



Figure 6.5 Carbon dioxide hydrate decomposition of hydrates that had been formed under high driving force.



2 IIII

Figure 6.6 Close up of figure 6.5 (b)

6.2 CONCLUSIONS

Macroscopic crystal morphology observations were made on methane and carbon dioxide hydrates on water droplets at 274.65 K. Two experimental pressures, 2150 and 1000 KPa, were used to demonstrate the effect of driving force. Each experiment was performed with two droplets approximately 5 mm and 2.5 mm in diameter or three droplets with a diameter of approximately 2.5 mm. It was found that all droplets in a given experiment would nucleate simultaneously and exhibited very similar surface morphology. Size of the droplet had no noticeable effect on nucleation time or

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macroscopic crystal morphology. On the other hand, it was found that the driving force affected the crystal morphology greatly. Under high driving force crystals nucleated much sooner. The surface was slightly jagged and numerous needlelike crystal extended themselves away from the hydrate-gas interface. Under low driving force, needle like crystals were not present and the surface was smooth and shiny under the lighting environment present. In most cases, hydrates did not nucleate under low driving force within 5 days and the experiment was concluded. In all experiments it was found that neither the droplet size or the hydrate forming gas had any effect on the macroscopic surface morphology. The final goal of this study was to monitor the decomposition of hydrates on water droplets. Independent of the initial driving force or hydrate forming gas, the hydrate crystals decomposed in much the same manner.

Chapter 7

A MORPHOLOGICAL STUDY OF STRUCTURE H HYDRATE

Studies on the morphology of structure H hydrate have been performed by employing the methane-neohexane-water system. Experiments were conducted on a water droplet approximately 5 mm in diameter immersed in a neohexane bath as seen in figure 2.9. The experimental temperature was set at 274.55 K and the pressures ranged from 4000 kPa to 5600 kPa to monitor the effect of driving force. The effect of dissolved neohexane in water on the solubility of methane in water was also investigated

7.1 STRUCTURE H MORPHOLOGY ON WATER DROPLETS

The kinetics of hydrate formation for the methane-neohexane-water system are significantly enhanced over those in the absence of neohexane as was noticed by Hutz and Englezos (1996). Hence, it was necessary to observe the rate of morphological change and check whether or not this exceeds that of structure I.

The experimental conditions with observed nucleation times are given in table 7.1. In addition the time elapsed after nucleation until the crystal structure became opaque is also given in table 7.1. The nucleation time was once again variable but influenced by the magnitude of the driving force. It was found that under high driving force (pressure equal to 5600 kPa) nucleation occurred within 61 min for two experiments and just over one day for a third experiment. On the other hand, a lower driving force yielded nucleation times equal to 890 and 703 min (two experiments). One

experiment that was performed at 4000 kPa did not nucleate within 5 days and it was terminated.

Another experiment was performed under high driving force in the absence of neohexane agitation. This experiment lasted 8 days without any hydrate activity and was terminated. The importance of agitation was discussed in section 2.1.6.2.

Table 7.1 Experimental conditions and nucleation times with observed times of when crystal structure became opaque. Experiments were performed with agitation.

•·	er jour brueture cerunite opuquer. Emperantenes store performent augustions							
T (K)	P (kPa)	Size (mm)	Nucleation (min)	Opaque (min)*				
274.65	5600	5	41	185				
274.65	5600	5	1752	39				
274.65	5600	5	61	180				
274.65	4500	5	890	48				
274.65	4500	5	703	56				
274.65	4000	5						

Time after nucleation time. For example it took 185 min after nucleation for the droplet in the first droplet to become opaque.

The morphology of structure H greatly differed from those experiments performed on structure I and described in chapter 6. Figure 7.1 shows a liquid droplet (7.1a) and its subsequent appearance with hydrates. The first stage of the morphology was a thin skin enveloping the water droplet as seen in figure 7.1b. This was quickly followed by a thickening of the hydrate on the surface as well as rapid localized growth at certain points on the water droplet as seen in figure 7.1c. These localized growths quickly surrounded the immediate vicinity while extending away from the droplet (figure 7.1d). The engulfed water droplet surrounded by hydrate then begins to buckle at the contact between Teflon-water as can be seen in figure 7.1e (bottom of the droplet). This site is





Time = $0 \min$ (a)



(c) Time= 1hour







Time=2 hours (d)











Chapter 7: A Morphological Study of Structure H Hydrate

hypothesized to be the site of lowest hydrate density since the concentration of dissolved gas and dissolved neohexane is impeded by the Teflon. The droplet covered by thick areas of hydrate continued to buckle, forming what seemed to be an inverted hyperboloid. This gap on the bottom of the droplet is a consequence of the disappearance of water inside the droplet that is being used to sustain hydrate formation. This disappearance is believed to occur through capillary rise of water through the porous hydrate. Figure 7.1f shows the water droplet covered in a dense layer of hydrate that impedes the transmittance of light (opaque). The appearance of opaqueness was visually noted in each experiment and the relevant data are given in table 7.1.

It is important to note that in one experiment needlelike formation did occur as in the morphology studies of structure I under high driving force. It is speculated that needles should have formed under high driving force for most cases of structure H. The reason that the needles did not form in most cases was probably due to the agitation of the neohexane surrounding the water droplet. This agitation caused shear around the droplet and would most certainly break off the fragile needle like formations extending radially away from the hydrate-covered surface. The reason that hydrates needle did form in this one case was probably due to the shape at which the hydrate formed. The shear was then reduced on the far side and allowed the growth of needle like crystals.

A measure of the kinetics of growth can be obtained by considering the time it took for the opaqueness to appear after the nucleation time. These data are given in table 7.1. It can be seen that after nucleation, the kinetics of hydrate growth on the water droplets is not dominated by the pressure but by the amount of time the neohexane has been exposed to the methane atmosphere (nucleation time). As seen, the longer the

nucleation time the earlier the appearance of opaqueness and hence the quicker the kinetics. This is most likely directly related to the availability (concentration profile) of methane in the neohexane. Unfortunately, this quantity was not measured since it was beyond the scope of this thesis.

One reformation experiment was conducted in order to ascertain how quickly the kinetics after nucleation were with the system having memory. This experiment was conducted on a 5 mm (diameter) droplet of water at 274.65 K and 5600 kPa. It took only 1 min for the nucleation to occur whereas it took 41, 61, and 1752 min in the experiments without memory (table 7.1). The opaqueness appeared in 45 min whereas in the experiment without memory it took 185, 39, and 180 min. It should be noted again that the measure of the amount of time required for the crystal to become opaque was a visual observation performed by the investigator. However, it does infer that the kinetics are much more rapid when the nucleation time is longer. It is believed that during this time more methane is dissolved in the neohexane and in the water. The solubility enhancement is discussed later.

Another difference between the morphology of structures I and H was the change in shape and size of the droplet after hydrate formation. In structure I the hydratecovered surface remained fairly spherical and in some cases appreciably reduced in size. In the case of structure H the crystal increased in size and distorted from the spherical shape as can be seen in figure 7.2. This could be a consequence of the rapid kinetics observed in structure H as well as the rapid localized growth observed. In structure I the hydrate seemed to behave uniformly whereas in structure H rapid areas of growth were observed in each experiment in random locations.


5mm Figure 7.2 Hydrate crystal with needle like crystals projecting radially away (T=1.5[°] C, P=5600 KPa)

7.2 EFFECT OF NEOHEXANE ON METHANE DISSOLUTION IN WATER

Experiments were carried out to investigate the effect of neohexane on the dissolution of methane in water. Three experiments were performed in pure distilled and deionized water at approximately 274.55 K and at 1150 KPa while three experiments were performed on water that had been saturated with neohexane. The average values are shown in table 7.2. The average moles of methane consumed in the absence of water for the three experiments was 0.00381 moles, while the average moles consumed in water initially contacted with neohexane was 0.00459 moles. This suggests that water saturated with neohexane increases the amount of methane consumed by approximately 17%. The reason that experiments were done at this pressure was because the three-phase

equilibrium pressure for structure H hydrates is approximately 1300 kPa at 274.6 K (Servio et al., 1999). Therefore experiments needed to be conducted below the methaneneohexane-water hydrate formation conditions to avoid any effect that possible hydrate formation might concur.

The above mentioned increase in the amount of dissolved methane gas provides evidence that structure H hydrate growth kinetics occur more rapidly in water saturated with neohexane. This is attributed to the enhanced concentration and hence availability of methane to participate in hydrate formation.

TABLE 7.2 Mole of methane dissolved in 150 cm³ of liquid water or liquid water saturated with neohexane.

T (K)	P (bar)	Neohexane Present	Moles	AAD**
274.55	11.50	NO	0.00381	0.00006
274.65	11.50	YES	0.00459	0.00008
274.48*	10.05	NO	0.00334	N/A

* Value from Lekvam and Bishnoi (1997)

** Average Absolute Deviation

7.3 CONCLUSIONS

Solubility experiments of methane in pure water were performed as well as methane in water that had previously been saturated with neohexane. Results show that the solubility of methane increases by approximately 17% in water presaturated with neohexane. Morphological experiments on structure H hydrate were carried out at pressures of 4000, 4500, and 5600 kPa. The experimental temperature was set at 1.5° C. It was found that driving force (deviation of experimental pressure from the three phase equilibrium pressure at a given temperature) had a large effect on the nucleation time but

did not significantly affect the rate of hydrate growth after nucleation. The rate of hydrate growth after nucleation seemed to be affected by the amount of time methane was allowed to dissolve in neohexane and hence the enhanced concentration of methane (available to form hydrate).

Chapter 8

CONCLUSIONS AND RECOMENDATIONS

8.1 CONCLUSIONS

Measurements were made on carbon dioxide dissolved in equilibrium with its hydrate as well as methane dissolved in water in equilibrium with its hydrate. Results show that the solubility decreases with decreasing temperature in the hydrate formation region. At pressures below hydrate forming conditions the solubility increases with decreasing temperature. Therefore, the existence of hydrates changes the normal solubility trend of methane and carbon dioxide with respect to temperature.

Laser light scattering experiments were performed on ethane hydrate in the absence and presence of monodispersed latex particles in order to test a new technique to study hydrate growth kinetics. The idea was to grow crystals on particles of know size, particle size distribution, and charge. This would eliminate the limitations of current laser light scattering techniques. The ethane system was chosen for convenience. The visually observed turbidity point was found to coincide with the rapid change in the photomultiplier voltage. The rate at which the photomultiplier voltage increased with the growth of hydrate particles could not be discerned as there was too many unknowns (size, shape, number of particles, effect of agitation, and if particles were growing on existing latex particles). Additional equipment such as an autocorrelator or spectrum analyzer is required in order to investigate the effect of latex particles on the growth of hydrate crystals.

Structure H is unique in comparison to that of structure I because (a) it requires a heavy component like neohexane and a light component such as methane (b) the equilibrium hydrate pressure is significantly lower than those of structure I and (c) the kinetics of hydrate growth are also quicker than those of structure I. It is also viewed as a potential storage mechanism for CH₄ gas because of the much more favorable operating pressures at which it can be formed. Furthermore, the ability for carbon dioxide to partake in structure H hydrate formation was tested by examining the methane-carbon dioxide-neohexane-water system. Structure H hydrate in the system consisting of 80% methane 20% carbon dioxide in the gas phase in contact with neohexane and water was found to form at pressure 1000 kPa below normal structure I forming conditions for methane hydrate at the same temperature.

Morphology studies on crystal nucleation and growth from water droplets were conducted. Structure I hydrate formation on water droplets was observed in the presence of methane and carbon dioxide. It was found for both gases that under high driving forces the nucleation time was quicker and the surface was covered under a jagged layer of hydrate with needle like crystals extending radially away from the center of the surface. Under low driving forces, nucleation times were longer and the hydrate surface was smooth and shinny with no needle like crystals present. After an extended time of growth it was found that the droplet collapsed in certain areas. This was taken as evidence that the hydrate-covered droplet does not stop hydrate growth.

Structure H crystal morphology was also examined for the methane-neohexanewater system using water droplets immersed in liquid neohexane and exposed to a methane gas atmosphere. It was found that the nucleation time depended on the driving

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force but the kinetics of hydrate growth were influenced by the amount of time that methane was allowed to dissolve into neohexane. In every case the crystal expanded in size and the apparent kinetics were significantly faster than those of structure I. Finally, the solubility of methane in water presaturated with neohexane was found to increase by approximately 17%.

8.2 CONTRIBUTION TO KNOWLEDGE

This work consists of several novel approaches and ideas that can aid in the understanding of many technological aspects concerning methane and carbon dioxide. Among these are the following:

- 1) The controversy in the literature concerning the solubility of carbon dioxide in water has been removed. This work focused on finding a reliable technique that could accurately measure the solubility of gas dissolved in liquid water in the presence of hydrates. It also confirmed theoretical calculations presented in the literature. This also gives valuable information on how disposing of carbon dioxide hydrate in the ocean floor will effect the natural solubility of carbon dioxide in water in the surrounding area. In addition, the present work on the solubility of methane in water in the presence of hydrate is the first reported in the literature.
- 2) Phase equilibrium data concerning the mixture of methane and carbon dioxide is important in order to predict whether hydrates may occur in oil reserves where these gas mixtures may come in contact with hydrocarbons such as neohexane. It was also important to illustrate how the composition of the gas

affected the hydrate equilibrium conditions (equilibrium pressure at a given experimental temperature). Another contribution to knowledge was the possible discovery of a hydrate structural change at equimolar concentration of methane and carbon dioxide below a certain temperature.

3) The first study of the morphology of structure I hydrate on multiple water droplets is credited to this work. Studies showed droplet morphology varied depending on the driving force. These morphological studies are required for the design of continuous crystallization process, which will convert water and gas into hydrate for storage and transportation purposes.

4) Structure H hydrates occur at much lower pressures than those of structure I. For this reason it is deemed as a good candidate for the storage and transportation of methane gas. The morphology of structure H hydrate gives valuable information on how the water droplets transform into hydrates. In the case for structure H the kinetics were visibly much more rapid and the droplet grew in size in contrast to structure I morphology. These observations are important in order to design safe technologies related to the transportation and storage of methane gas.

8.3 **RECOMMENDATIONS FOR FUTURE WORK**

Several important points have not been investigated in this study and need to be addressed in the future. They are as follows:

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- 1) In order to model the kinetics of hydrate growth of structure H the solubility of methane in neohexane and water and in the presence of hydrates must be determined in detail.
- 2) It is important, for modeling purposes, to know the mutual solubility of water and neohexane liquids in each other. Research into determining the partition coefficient of methane in neohexane and water must be performed.

3)

4)

- The laser light scattering technique given in this work has not yet been fully tested. It is important to pursue these kinetic experiments on latex particles, as they will give great insight into the growth behavior and particle size distribution of hydrate crystals. Necessary equipment would include an autocorrelator or a spectrum analyzer.
- Another important future recommendation that complements point 3 would be to enhance the digital imaging device. It would be of great benefit to have higher magnifications microscopes, up to 100 X, coupled with image analyzing software. This would allow us to monitor growth and shrinkage rates of water droplets, depending on the structure, and give valuable information required in determining mechanisms of growth and decomposition.
- 5) Morphological studies on pure systems that form structure I and structure H are presented in this work. It is important now to focus the attention on adding inhibitors to water droplets and monitoring their morphology under growing and decomposing conditions. This would give valuable information on selecting and testing newly developed inhibitors for hydrate prevention.

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- 6) This work has provided information backing up the fact that structure H hydrate is a powerful alternative to storing and transporting natural gas. The morphology experiments show that the water significantly converts to hydrate consuming any methane and neohexane in the vicinity. It is therefore important to further this research to develop a process that takes advantage of this behavior.
- 7)
- A structural change in the hydrate crystal is believed to have occurred in the equilibrium study of equimolar methane and carbon dioxide in contact with neohexane and water. This work should be continued and Raman spectroscopy or x-ray diffraction should be implemented in order to confirm this postulation.

Appendix A

Error Analysis of Solubility Measurement

The solubility of gas dissolved in equilibrium with its hydrate is given as follow,

$$x_{eq} = \frac{\frac{x_g^R n_{H2O}}{1 - x_g^R} + n_{Exp}^G}{\frac{x_g^R n_{H2O}}{1 - x_g^R} + n_{Exp}^G + n_{H2O}}$$
(3.2)

where

$$n_{Exp}^{G} = \left(P - P_{H2O}^{V}\right) \frac{V}{ZRT}$$
(3.1)

The following equation was used to calculate the uncertainty in the methane and carbon dioxide solubility experiments in the presence of gas hydrates (Coleman and Steele, 1999). It is as follows:

$$x = r(P, T, x_g^R, n_{H2O}, V)$$
(A.1)

$$U_{r}^{2} = \left(\frac{\partial r}{\partial T}\right)^{2} U_{T}^{2} + \left(\frac{\partial r}{\partial P}\right)^{2} U_{P}^{2} + \left(\frac{\partial r}{\partial x_{g}^{R}}\right)^{2} U_{x_{g}^{R}}^{2} + \left(\frac{\partial r}{\partial n_{H2O}}\right)^{2} U_{n_{H2O}}^{2} + \left(\frac{\partial r}{\partial V}\right)^{2} U_{V}^{2}$$
(A.2)

where U_T , U_P , U_{XgR} , U_{NH2O} , and U_V are the uncertainties in the measured variables and U_r is the uncertainty in the solubility measurement. The following derivatives are then inserted into equation A.2 in order to calculate the uncertainty in the solubility of methane and carbon dioxide dissolved in water.

$$\frac{\partial r}{\partial X_g^R} = \frac{(TRZNw)^2}{(VP - VPX_g - VP_v + VP_v X_g + NwZRT)^2}$$
(A.3)

$$\frac{\partial r}{\partial P} = \frac{NwTRZ(-1+X_g^R)^2 V}{\left(VP - VPX_g - VP_v + VP_v X_g^R + NwZRT\right)^2}$$
(A.4)

$$\frac{\partial r}{\partial T} = \frac{NwRZ(-1+X_g^R)^2 (P-P_v)V}{\left(VP - VPX_g - VP_v + VP_v X_g^R + NwZRT\right)^2}$$
(A.5)

$$\frac{\partial r}{\partial Nw} = \frac{(-2X_g^R + PX_g^{R^2} + 2P_v X_g^R - P_v X_g^{R^2} + P - P_v)VTRZ}{\left(VP - VPX_g - VP_v + VP_v X_g^R + NwZRT\right)^2}$$
(A.6)

$$\frac{\partial r}{\partial V} = \frac{NwTRZ(-1+X_g^R)^2 (P-P_v)}{\left(VP - VPX_g - VP_v + VP_v X_g^R + NwZRT\right)^2}$$
(A.7)

Sample Calculations of the Error in CO₂ solubility measurement

A program was written in the Matlab language that used equations A.2-A.7 to compute the uncertainty in the solubility measurement. The input values to the program along with the uncertainties are as follows for the experimental conditions of T=274.15 \pm .1K and P=37 \pm 0.15 bar:

Table A.1

Variable	Value	Uncertainty
Р	100.22 KPa	0.15KPa
Т	20.0°C	0.1°C
X ^R g	0.704E-3	0.1%
Pvp	2.2 KPa	NA
V	229 cm^3	0.2%
Nw	.577 moles	0.02 moles
X	0.0158	To be computed
Z	1.02	NA

The uncertainty in the solubility was then calculated to be 3.41%

Average Absolute Deviation for methane dissolution in water presaturated with

neohexane

$$AAD = \frac{\sum_{i=1}^{N} \left(\left| Y_i - \bar{Y} \right| \right)}{N}$$
(A.8)

where Y_i is the measure value, \overline{Y} is the average value, and N is the number of data points collected.

Appendix B

Laser Light Scattering and its Application to Hydrates

It has been a standard technique since the mid 1960's to use laser light scattering to determine the shape and size of molecules in solution. This is done through a measurement of intensity. With the development of lasers it has become possible to determine the spectrum of light scattered, which contains information related to the hydrodynamic properties of the scatters, such as the translational and rotational diffusional coefficients. Credit for the first theoretical analysis of the scattered spectrum is given to Komarov and Fisher and Pecora independently in 1963 (McQuarrie, 1976). In 1964 the study of light scattering was applied to dilute solutions of polystyrene latex particles, which showed good quantitative agreement with theory.

In this section the theory of light scattering will be applied to determining the size of hydrate particles grown on polystyrene latex spheres in solution. It should be noted that this chapter is just a brief summary to the broad and complex topic of light scattering. In order to obtain a good understanding of the subject one should have a good background in electromagnetic waves and radiating system, a good book on the topic being by Jordan and Balmain in 1968, as well as in statistical mechanics, recommended reading of Mcquarrie in 1976.

Introduction to laser light scattering

Consider a volume v, which contains N identical scatters in a nonscattering solvent. If this scattering volume is then irradiated with a monochromatic plane wave of

frequency w_o , the light scattered through an angle θ by the jth scatterer is given in complex notation by (McQuarrie, 1976)

$$E_{i} = A_{i}(t)e^{i2\pi\phi_{j}}e^{-iw_{0}t}$$
(B.1)

where $A_j(t)$, is the amplitude of E_j , and may depend on the orientation of the scatterer



Figure A.1 The geometry used to calculate the intensity of radiation scattered through an angle θ . Plane A represents the incident radiation, and B represents the observer's plane. (Mcquarrie, 1976)

From vector calculus and the above diagram it can be shown that

$$2\pi\phi_j = \frac{2\pi n}{\lambda_0} (\vec{u}_0 - \vec{u}) \bullet r_j = \kappa \bullet r_j$$
(B.2)

where n is the refractive index, λ_0 is the wavelength of the radiation in solution, and θ is the scattering angle. The above variables are taken as values of the solution, which is mostly solvent. The magnitude of κ , the scattering vector, is the following

$$\kappa = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2} \tag{B.3}$$

Now we may right the energy for the total scattered field at a large distance R from the scattering volume as

$$E_s = \sum_{j=1}^{N} A_j(t) e^{i\kappa \cdot r_j} e^{iw_0 t}$$
(B.4)

The total average intensity is given by the time average of the square of the total energy of the scattering

$$I_{s} = \left\langle \left| E_{s} \right|^{2} \right\rangle \tag{B.5}$$

Introduction to the light scattering experiment

There are two different types of light scattering experimental techniques that are used in deterring the small frequency shifts that result because of the scatter's. These involve the so-called optical mixing techniques developed by Cummins et al in 1969 (Mcquarrie, 1976). The first optical mixing technique is the homodyne method where the scattered spectrum is mixed with itself while the heterodyne method is the technique used when the scattered spectrum is mixed with part of the incident beam, see figure 16. Both methods obtain the same required spectrum information but use different methods in order to determine the scattered spectrum, therefore for this study we shall focus on the homodyne method that is simpler to use.



Figure A.2 Schematic of Light Scattering Apparatus (Nerheim et al, 1992)

Photon Correlation Spectroscopy for Monodisperesed Spherical Particles

In a homodyne experimental technique the intensity of the scattered radiation is observed at the cathode of a photomultiplier. Either a real time autocorrelator or a spectrum analyzer reads the output from the photomultiplier. If a real time autocorrelator is used, the intensity autocorrelation function of the output current of the photomultiplier is calculated by the following

$$G^{(2)}(j\Delta\tau) = \langle n_i, n_{i+j} \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^N n_i n_{i+j}$$
(B.6)

where $\Delta \tau$ is the sampling time, N is the total number of samples, $j\Delta \tau$ is the autocorrelation delay time also expressed simply as τ , j is the number of correlator channels, and n_i is the number of photons counted in sample *i*. It should be noted that the

number of photons counted is proportional to the current since the current is a measure of photons per second, therefore current may be used in place of photons counted without any change in the results.

At long delay times the intensity autocorrelation approaches a baseline value expressed as

$$G^{(2)}(\infty) = \langle n \rangle^2 \tag{B.7}$$

With this result the intensity autocorrelation function can be normalized to give the net intensity autocorrelation function, which is

$$g^{(2)}(\tau) = \frac{G^{(2)}(j\Delta\tau)}{G^{(2)}(\infty)} = \frac{\langle n_i, n_{i+j} \rangle}{\langle n \rangle^2}$$
(B.8)

Now if we assume that the optical field is a Gaussian random process, then the Siegert relation applies (Nerheim et al, 1992):

$$g^{(2)}(\tau) = 1 + \beta |g^{(1)}(\tau)|^2$$
(B.9)

where β is dependent on the optics and has a magnitude between zero and one

$$0 \prec \beta \prec 1 \tag{B.10}$$

 $g^{(1)}(\tau)$ is the net electric field autocorrelation function and is dependent on the Fourier Transform of the fluctuating density of particles, \hat{n}_d . It is given by the following relation

$$g^{(1)}(\tau) = \left\langle \hat{n}_d(\kappa, t), \hat{n}_d(\kappa, 0) \right\rangle \tag{B.11}$$

where κ is the scattering vector derived at the beginning of this section. Fick's first and second laws of mass conservation can relate the fluctuating density of particles to the diffusion coefficient, D as follows

$$\hat{n}_d(\kappa,t) = \hat{n}_d(\kappa,0)e^{-\kappa^2 Dt}$$
(B.12)

Upon substitution of equation (B.12) into equation (B.11) we obtain a new relation for the net electric field autocorrelation function

$$g^{(1)}(\tau) = S(\kappa)e^{-\kappa^2 Dt}$$
(B.13)

where S(k) is the static structure factor (Nerheim et al, 1992) and is defined as

$$S(\kappa) = \langle \hat{n}_d(\kappa, 0) \rangle^2 \tag{B.14}$$

For a dilute suspension of monodispere spherical particles where the motions of the particles are uncorrelated the value of the static structure factor becomes unity for all values of the scattering vector.

By fitting the experimental data to $g^{(2)}(\tau)$ the electric field autocorrelation function can be deduced form equation (B.9). The baseline value of the intensity autocorrelation function is then measured experimentally. With the above results and using equation (B.13) the diffusion constant can be calculated. Under the assumption that the particles are spherical, non-interacting, freely diffusion Brownian particles, the free translational diffusion coefficient, D, can be related to the diameter, d, of the particles by using the Stokes-Einstein relation listed below

$$d = \frac{k_B T}{3\pi D\eta} \tag{B.15}$$

where d is the hydrodynamic size, which includes any matter which moves with the particle such as coating , solvation layer, surfactants, or the growth of the particle due to swelling. k_B is the boltzman's constant, T is the absolute temperature, and η is the viscosity of the suspending fluid.

Photon Correlation Spectroscopy for Polydisperesed Spherical Particles

If the sample to be analyzed consists of particles of different sizes it is said to be polydisperesed. The electric field autocorrelation function then consists of a distribution of exponentials and is calculated by the following integral

$$g^{(1)}(\tau) = \int_{0}^{\infty} G(\Gamma) e^{-\Gamma \tau} d\Gamma$$
 (B.16)

where

$$\Gamma = \kappa^2 D \tag{B.17}$$

where κ is the scattering vector previously defined and D is the diffusion constant of the particles in solution. In order to evaluate equation (B.16) the value of β must be

calculated. β must be deduced from either experimental data by a fitting procedure or in normalizing $G(\Gamma)$.

The discussion will now be focused on how to invert equation (B.16) in order to obtain $G(\Gamma)$. If we take $\sqrt{(g^{(2)}(\tau)-1)}$ and plot it vs. the delay time τ , the following expression is obtained

$$\sqrt{\beta} |g^{(1)}(\tau)| \tag{B.18}$$

For a polydispersed system Cummins and Pusey in 1977 (Nerheim et al, 1992) found that $g^{(1)}(\tau)$ could be expressed as

$$\left|g^{(1)}(\kappa,\tau)\right| = \frac{\sum_{j} N_{j} \left|S_{j}(\kappa)\right|^{2} e^{-\Gamma_{j}\tau}}{\sum_{j} N_{j} \left|S_{j}(\kappa)\right|^{2}}$$
(B.19)

The scattering angle remains constant therefore the scattering vector is also constant, therefore the above expression may be reduced to the following series of exponential functions, each with a different amplitudes, a_i

$$g^{(1)}(\tau) = a_1 e^{-\frac{\tau}{\tau_1}} + a_2 e^{-\frac{\tau}{\tau_2}} + a_3 e^{-\frac{\tau}{\tau_3}} \dots$$
(B.20)

The different delay times can now be found by fitting the experimental data to the above equation where τ is the delay time and τ_i is the relaxation time for the corresponding

particle diameter, d_i . The relative scattered intensity from the particles with a diameter d_i is given by

$$I_i = \frac{a_i}{\sum a_i} \tag{B.21}$$

and the different particle size diameters are then found by

$$d_i = \tau_i \frac{K_B T \kappa^2}{3\pi\eta} \tag{B.22}$$

 τ_i and a_i are found by using any various fitting procedure or mathematical package such as Mathematica or Matlab.

🚣 TBFUGA		_ 🗆 🗵	
T & P of Fluid	TB properties for component		
Temperature 25 C -	d (m^3/kmol)	0.02564	
Pressure (bar) 1.01	Zc	0.31135	
Component	q1	0.36438	
CH4	q2	0.05927	
Volume	Tc (K)	190.555	
Gas 1.5267596311	Pc (kPa)	4595	
Liquid 1.5267596311	Molecular Weight (kg/kmol)	16.04	
Fugacity (bar) Gas 1.007796895 Liquid 1.007796895	Action Calculate	Cancel	

Appendix C

Fig C.1 Screenshot of program TBFUGA which calculates the pure component molar volumes for water, methane, ethane and carbon dioxide as well as the pure component fugacities.

P-T-V Data		Time (s)	⊂ Moles	
Temperature (C)	Pressure	Interval 2	0	m^3/kmol
T1 0	Patm (mm Hg) 760	Elapsed 0	0	moles currently
T2 0	Patm (kPa) 101.3	Clabus	0	moles initial
T3 0	Pcell (kPa)	Waiting	0	moles consumed
TR 0	volume R1 [252	Component	Fugacity in bar	
		C02 •	0	
itart Date & Time —				
11/ 8/01 -	Filename	Action	Chart Turbida	1
	c:/windows/desktop/run.>	ds		
10:12:53 AM			Pause Befresh	calculate

Fig C.2 Screenshot of program Hydrate P-T records the temperature and pressure as well as the moles consumed during a gas consumption experiment.

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