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THERMODYNAMICS AND KINETICS STUDIES OF FORMATION AND DECOMPOSITION OF CLATHRATES HYDRATES OF METHANE, CARBON DIOXIDE AND THEIR MIXTURES USING A DIFFERENTIAL HEAT FLUX CALORIMETER

by

GUILLAUME BESNARD

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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ABSTRACT

Thermodynamics and Kinetics Studies of Formation and Decomposition of Clathrates Hydrates of Methane, Carbon Dioxide, and Their Mixtures using a Differential Heat Flux Calorimeter

by

Guillaume Besnard

A high pressure heat flux calorimeter in isobaric, temperature-ramping mode has been used to measure the solubility of pure methane, pure carbon dioxide and methane-carbon dioxide mixtures. The solubility measurements emphasize a crystallization-like process taking place during hydrate formation and show a striking divergence from Henry's Law, the frequently used calculation procedure, prior to and during hydrate formation. These measurements were further used to determine the enthalpies of solution/dissociation, and entropies change. Moreover, the hydration numbers of these compounds provide some explanations and criteria of stability of the cages of gas hydrates in the host lattice.

Finally, a kinetic study confirms the crystallization process of hydrate formation and exhibits a high level of supersaturation prior to hydrate formation and also a high consumption rate during hydrate formation.
ACKNOWLEDGEMENTS

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INTRODUCTION

Gas hydrates, which are included in the broad classification of the clathrate compounds, are ice-like structures formed from gases and a large excess of water under suitable conditions of temperature and pressure. Introduced by Powell in 1948, the term “clathrates” is a structural combination of two substances which remain associated, not through strong attractive forces, but because strong mutual binding of the molecules of a non-polar or low polarity, makes possible the firm enclosure of the former, and whose self-assembly is aided by the other, as shown in Figure 1.

Suitable conditions usually involve moderate to low temperature and high pressure where the supply of gas is sufficient to initiate and stabilize the hydrate structure. Therefore, with the exception of natural gas hydrates, the thermodynamic conditions required for stability rarely make the clathrate hydrates occur on the earth's surface. However, the existence of “air hydrate” in the Antarctic ice cover has been proposed by Miller in 1969 in order to justify the presence of air found in ice cores taken at depths greater than 1200 m. Miller has even considered the possibility that gas hydrates might be present in abundance in other parts of the solar system. For instance, methane hydrate, though not proven, might be found on Uranus, Neptune, Saturn and Jupiter.
Figure 1. Aggregation of a Short Lived Water Molecule From High Temperatures To Low Temperatures
(Source: Makogon, 1974)

Figure 2. Schematic Diagram of a Reservoir Containing both Hydrates and Gas
(Source: Cox, 1983)
The necessary conditions of pressure and temperature are met on earth in shallow sediments located less than 2000m deep in two regions. The first one is the continental region at high latitudes where the surface temperatures are very cold, e.g. below 0°C. The second one is the submarine continental region where the water is not only cold, around 0°C, but the pressures are also very high, above 3 MPa. Therefore, gas hydrates are found where temperatures are cold enough for onshore and offshore permafrost to be present like in polar regions, Northern Russia or North America Arctic. Figure 2 shows the diagram of a reservoir containing both hydrates and gas.

Studies of gas hydrates go back to 1810 when Humphrey Davy, in the Bakerian lecture to the Royal Society, explained that an aqueous solution of chlorine froze at a higher temperature than water itself. He has been followed by Villard and de Forcrand, two French scientists, who became the most prolific hydrate researchers of this early period. Villard discovered the existence of methane, ethane and propane hydrates in 1888, while de Forcrand tabulated the equilibrium temperatures for fifteen components in 1902. In the mid-1930’s, the gas hydrates turned out to be one of the most important research areas among the scientists since mixed hydrates (hydrates of more than one component) had been found to be responsible for the plugging of pipelines, frequently at temperatures above the ice point. As a pioneer of these researches, Hammerschmidt in 1934 reported that the separation of the hydrates as solids might be influenced by secondary factors like the gas flow rate or the pressure fluctuations.
Shortly thereafter, Katz and co-workers undertook both experimental and correlational work to predict their formation/decomposition conditions. In 1946, Deaton and Frost published their results on the prevention of hydrate formation by using gas dehydration or the addition of specific inhibitors. Most of the current predictive techniques are still compared to the data of their study. They were followed by Bond and Russel in 1949, Kobayashi et al. in 1951 and Woolfolk in 1952 and it appeared that methanol was one of the most efficient inhibitors since it becomes concentrated in the free water phase after being vaporized into the gas at some upstream point.

In 1949, using an X-ray diffraction experiment, Von Stackelberg and Muller determined a cubic structure for the gas hydrates. But Claussen in 1951 was the first to conceive the idea of the packing of pentagonal dodecahedra into a diamond lattice, now known as structure II. Then Claussen and Muller deduced from X-ray diffraction that the gas hydrates did not all conform to structure II and hence formulated a second structure I, a body-centered cubic lattice. This lattice was verified by Pauling and Marsh in 1952 with the study of chlorine hydrates. Table 1 gives the specifications of these structures while Figure 3 shows a unit cell for each structure and Figure 4 classifies the size of the different molecules. Structure I is formed by the linkage of 46 water molecules where two pentagonal-dodecahedral cavities are surrounded by 20 water molecules and six tetrakaidecahedral cavities by 24 water molecules.
Structure I
(Source: Makogon, 1974)

Structure II
(Source: Makogon, 1974)

Structure H
(Source: Metha and Sloan, 1996)

Figure 3. Unit Cell of a Gas Hydrate of Structure I, II and H
Figure 4: Size of Different Molecules and Their Hydrate Structures
(Source: Christiansen and Sloan, 1994)
Structure II consists of 136 water molecules, enclosing 16 pentagonal-dodecahedral surrounded by 20 water molecules and 8 hexakaidecahedral cavities by 28 water molecules. Structure I has been best defined by McMullan and Jeffrey in 1965 for the ethylene oxide hydrate and structure II by Mak and McMullan in 1965 for H₂S using X-ray diffraction techniques.

Table 1. Hydrate Crystal Cell Structures

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<thead>
<tr>
<th>Hydrate crystal structure</th>
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<th>II</th>
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<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Lattice description</td>
<td>Body Centered</td>
<td>Diamond</td>
</tr>
<tr>
<td>Cavity Description</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Description</td>
<td>5₁²</td>
<td>5₁²₆²⁺</td>
</tr>
<tr>
<td>Number of cavities</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Average cavity radius, Å</td>
<td>3.91</td>
<td>4.33</td>
</tr>
<tr>
<td>Coordination number¹</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Ideal unit cell formula</td>
<td>6X.46H₂O</td>
<td>8X.136H₂O</td>
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¹ Number of oxygens at the periphery of each cavity

(Source: Sloan, 1990)

In 1959, Van der Waals and Platteeuw in their comprehensive treatment of solid clathrate solutions described the nature of gas hydrates as a solid solution in which gas molecules occupy cavities in a framework of tetrahedrally coordinated water molecules linked together by hydrogen bonds.
Saito, Marshall and Kobayashi confirmed this theory in 1964 by proving that the solid solution theory could be applied above the ice point for gas hydrates, and Galloway and Kobayashi later determined the hydration numbers for methane hydrate.

Until 1987, molecules larger than n-butane were considered to be non-hydrate formers. Some molecules such as isopentane or methylcyclopentane were assumed to be non-hydrate formers by Katz et al. or sll formers by Lippert et al. Therefore, the discovery of the structure H by Ripmeester and Ratcliffe using X-ray diffraction and Xe NMR studies in 1987 led to a tremendous change of hydrate perspectives. They identified 24 hydrocarbon molecules which could stabilize structure H hydrates. This structure is usually composed of two guest species, as shown in Figure 3.

By using a differential high pressure heat flux calorimeter built at Rice University by John Lievois in 1987, temperature ramping, isobaric experiments have been conducted successfully for different gases, after some important modifications of the control/data acquisition system. Throughout the experiments, the solubilities of hydrocarbon gases in liquid water at low temperatures and high pressures have been determined in the vicinity of the hydrate formation conditions. They supplemented the scarce data available in the literature due to experimental difficulties usually encountered in the appearance of a multitude of phases.
Throughout this work, a better understanding of the hydrate formation/decomposition conditions is provided, including sets of very useful informations on some derived thermo-physical properties such as the enthalpy and entropy of the phase changes. The hydration numbers for the pure components, methane and carbon dioxide, are also studied and yield explanations on the stability of the cages.
A. EXPERIMENTAL METHOD

A.1. PREVIOUS EXPERIMENTAL METHODS

Over fifty years, the development of successful apparatuses for hydrate phase equilibrium studies has been guided by three principles. Two types of apparatuses have been used according to these principles, a visual cell apparatus and more recently a differential calorimeter. The three principles are the following:

A.1.1 VIGOROUS AGITATION

As explained by Villard in 1888, vigorous agitation is necessary to obtain complete hydrate conversion. First of all, the agitation provides surface renewal and an exposure of liquid water to the hydrate former. Secondly, it prevents any occlusion of water within the hydrate mass. Finally, Hammerschmidt, in 1934, explained that the agitation in the form of flow fluctuations, pressure cycles or bubbling gas through the water was necessary to initiate hydrate formation and therefore decrease its metastability.

A.1.2 PREVENTING HYDRATE METASTABILITY

It has been shown that some hydrate metastability is always present during its formation. However, metastability seldom occurs with slow heating or depressurization during hydrate dissociation.
Therefore, the endpoint of hydrate dissociation is taken as an indication of the upper limit of existence or metastability. In 1942, Carson and Katz confirmed the theory that the dissociation condition is considered as the hydrate equilibrium point, by studying the solid solution behavior of hydrates formed by gas mixtures.

A.1.3 Isochoric Apparatus

A change in pressure confirms the gas hydrate formation or dissociation in an isochoric apparatus. The dissociation of the last hydrate crystal by slow heating shows a decrease in the slope of the pressure versus temperature locus. Moreover, the pressure and the temperature are recorded and the final hydrate decomposition temperature is taken as the intersection between the cooling and the heating curves.

Two main apparatuses have been used following these principles.

A.1.4 Visual Cell Apparatus

In 1934, Hammerschmidt constructed a flow apparatus for the simulation of hydrate formation in pipelines. It consisted of a thermostatted pyrex tube where hydrates were visually observed. He was followed in 1937 by Deaton and Frost who built a static hydrate equilibrium apparatus. Our apparatus has been developed over the past fifty years according to Carson and Katz in 1942, Makogon in 1974, Vysniauskas and Bishnoi in 1983 and more recently, by Feney-
rou and Song at Rice University in 1996. The heart of the apparatus consists of a sight glass in which hydrate formation and dissociation could be visually observed. Only a fraction of the void space is filled with water, the remainder is made up of gas and hydrate. The cell is enclosed in a thermostatted air bath. Please refer to Feneyrou's Thesis for more details.

A.1.5 DIFFERENTIAL CALORIMETER

The purpose of this work has been to determine the temperature of formation/dissociation as well as the heat of dissociation. It has been defined as the heat required to transform crystalline hydrates into fluid phases: gas and liquid water. For almost a century prior to any calorimetric measurements, the heats of hydrate dissociation have been indirectly determined via the Clausius-Clapeyron equation by differentiation of the three-phase equilibrium pressure-temperature data:

$$\frac{d\ln P}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H_d}{zR}$$

where P and T are the absolute pressure and temperature of hydrate equilibrium with vapor and liquid water, R is the universal gas constant and z is the compressibility factor.

However, as Sloan and Fleyfel explained in 1992, the use of the Clausius-Clapeyron equation does not provide the most accurate value for the heat of dissociation.
Moreover, there is an inherent difficulty with this equation when there is significant non-stoichiometry, as is the case for molecules which occupy the smaller cavity. Finally, even if this equation provides acceptable estimates of the heat of dissociation, no information concerning the hydrate heat capacity is directly given by that equation.

Three decades earlier, Glew, Barrer, van der Waals and Platteeuw explained that this equation was only valid for an univariant system and the reaction had to follow three rules:

* The fractional occupation of each cavity by the guest molecules should not change.

* The condensed-phase volume changes should be negligible relative to the gas volume.

* The gas composition should be constant.

Therefore, the most accurate way to determine the heat of dissociation is to measure it via a calorimeter. Such measurements are painstaking and hence limited in number. Recently, three experimental techniques using a calorimeter have been applied to measure the hydrate heat capacity and dissociation enthalpy: Handa in 1986, Lievois in 1987 and Rueff in 1988. These works reflect a growing interest in the thermal properties of hydrates.
The calorimeter, used for this work, was developed by Lievois in 1987. This apparatus was designed to measure various thermophysical properties of natural gas hydrates such as heat capacities or formation/dissociation enthalpies of gas hydrates. The technique used is a dissociation one, which is based on varying the total volume under isothermal conditions.

A.2. ISOBARIC TEMPERATURE-RAMPING EXPERIMENTS

The differential calorimeter can be operated in three modes, isochoric, isothermal and isobaric temperature-ramping; but this work has been restricted to the isobaric temperature-ramping experiments.

A.2.1 ISOCHEMIC MODE

When the system is at constant volume, pressure changes invariably accompany the temperature scan. In case of hydrate dissociation, the pressure changes may be important. Therefore, this might be disadvantageous calorimetrically since an increase in the system pressure makes a larger temperature scan necessary to prevent the hydrate dissociation from ceasing. The temperature of the closed cell is lowered from the liquid-vapor region and the cooling decreases the pressure slightly. The temperature is then slowly increased in order to dissociate the hydrates.
The path followed due to the increase in temperature must stay along the three-phase line, $L_w-H-V$, since there is only one degree of freedom as given by Gibbs Phase Rule: $F=C-P+2$, where $F$ is the degree of freedom, $C$ is the number of components (2: methane-water or carbon dioxide-water) and $P$ is the number of phases (3: $L_w-H-V$). The system will follow this locus until all the hydrate is dissociated, according to the Phase Rules.

**A.2.2 ISOTHERMAL MODE**

In 1987, Lievois used this mode to determine the enthalpy of dissociation for the methane hydrates at two temperatures, 5 and $10^\circ$C; typical temperatures for hydrate recovery schemes or natural gas processing. Dissociation is initiated by withdrawing the plungers, hence increasing the total system volume. This reduces the pressure, thus dissociating the hydrates. At the three-phase conditions, the pressure will remain constant until the hydrates are depleted.

**A.2.3 ISOBARIC MODE**

The system is maintained at a constant pressure by using the pumps. The temperature is decreased until hydrate forms from the gas and liquid phases. After hydrate formed, the temperature is slowly increased until the last crystal disappears. This mode has been used for our work with the following gases: methane, carbon dioxide and a mixture methane-carbon dioxide.
A.3 OBJECTIVES OF THIS WORK

This work intends to provide information on the solubility of different gases in the liquid phase at temperatures in the vicinity of the hydrate formation conditions. This allows the determination of the enthalpy of solution/dissociation and the accompanying entropy changes. Moreover, the determination of the hydration number will provide some explanations as to the stability of gas hydrates. Finally, a study of the Methane-Carbon Dioxide-Water system has been conducted at 560 Psia in order to obtain a better understanding of the thermodynamic behavior of mixtures.

A.4. EXPERIMENTAL PROCEDURE

The right cell of the calorimeter shown in Figure A.1 is first cleaned with ultra-pure water (17.0 megaohm-cm resistance) and evacuated to remove the air. Then the system is charged with roughly 650 grams of very dilute aqueous potassium chloride solution (approximately 0.004 normal). The solution is prepared from ultra-pure water and Baker Analyzed Reagent grade potassium chloride (assay 99.7%). These 650 milliliters of solution fill approximately two thirds of the cell in order to insure that the electrical conductivity cell will be immersed and that the magnedrive propellers will achieve a vigorous mixing of the cell contents.
Figure A.1. Block Diagram of the Twin Cells of the Heat Flux Calorimeter

(Source: Lievois, 1987)
A small amount of methane gas is introduced into the system which includes the calorimeter cells, the right pump and the pressures lines. The system is evacuated again and charged with methane gas to the desired pressure. After eliminating all gas leaks, the temperature in the bath and in the cell are recorded until reaching thermal equilibrium. It usually takes 10 to 12 hours to achieve this multiphase equilibrium.

The next step is the temperature-ramping at a constant rate where the pressure is controlled via a digital pump. A temperature controller automatically sets the cooling/heating rate; finally reaching the desired temperature during the cooling/heating phase.

The computer controls the block/cell temperatures and monitors the various independent parameters during the formation/decomposition of the Methane hydrate gas. In this procedure, the fundamental measurement is the displacement of the digital pump, controlled by the stepping motor. The stepping motor is actuated by a digital-based driver which is controlled by the computer via the IEEE interface. Therefore, the pump is able to withdraw or add gas to or from the cell at very precise cooling/heating rates, from 0.6°C/hr to 6.0°C/hr.

The displacement of the pump gives us the volume of methane gas added to the cell, hence the solubility of methane in pure water. The computer controls the pressure every four seconds and the data acquisition is performed every minute, allowing very precise control of the temperature-ramped, isobaric
experiment. Appendix A shows a listing of the Visual Basic program and the flow-sheets for each device measurement. The automation of the apparatus allows very long experiments lasting several days. Since the elapsed time is known for the isobaric experiments, the apparatus can also be used for slow kinetic experiments, without differentiation.

These high pressure experiments might induce gas leaks which have to be detected and eliminated prior to the experiment. Most of the glitches which occur during the experiments are controlled by linkage to the computer and therefore do not affect the temperature-ramping, especially considering glitches from the pressure transducers.

Although the phase behavior of gas hydrate is relatively well-known, hydrate formation might be difficult to achieve because of its proclivity to show metastability. The technique which has been discovered to control the hydrate formation involves a combination of supercooling and agitation via the magnetic stirrer [Lievois, 1987]. In order to maintain a constant water-gas contact, hydrate formation requires sufficient agitation on the order of 60 RPM of stirrer shaft speed. Once a series of isobaric experiments with methane had been conducted, the liquid solution is removed and the cell is cleansed with ultra-pure water. Then, the system is evacuated for the next charge of gas at a desired pressure.
B. EXPERIMENTAL APPARATUS

The hydrate formation and decomposition takes place in a differential calorimeter which was developed by Lievois in 1987, a decade ago. This calorimeter is commonly known as a heat flux calorimeter. The apparatus consists of the calorimeter itself, the pressure network, the temperature control and the computer/data acquisition network.

B.1. CALORIMETER

The calorimeter is a twin calorimeter, consisting of two symmetrical cells which are both insulated from a surrounding aluminum block. Figure B.1 shows the components of this calorimeter. The operating temperature range is from -40°C to 250°C. The cells have an internal volume of roughly 1 liter and a pressure rate of 10,000 Psi. The right cell serves as a sample cell while the left cell serves as a reference cell, allowing differential measurements of the temperature or an absolute one. Although the theory is based on identical cells, the experiments require slightly different cell designs. The right one is used for “free surface” experiments while the left one is used for “porous media” experiments. The heat produced or consumed during the experiment will induce a temperature change in the cell. Any heat exchange will occur almost exclusively by conduction since radiative and convective components are minimized by design in order to quantitatively relate the total heat flux to the local temperature difference.
Figure B.1. Block Diagram of Pressure System and Valves Network of the Calorimeter

(Source: Lievois, 1987)
The thermopiles measure this local temperature difference between
the sample cell and the surrounding block.

B.1.1 THERMOPILES

Each thermopile consists of 180 copper-constantan thermocouples
hooked up in series. In each thermopile, there are nine levels of twenty junctions-
"stars" equally spaced around the sample cell. The resulting differences in voltage
for the two thermopiles represent the differential heat flux for the two cells. Inte-
grating this voltage over time gives the total heat transfer associated with the
"events". For a more in depth explanation, please see Lievois’ Thesis. The mea-
surement are conducted with a HP 3458A multimeter.

B.1.2 ELECTRICAL CONDUCTIVITY CELL

The internal electrical conductivity cell is used to track the amount of
water in the hydrate and liquid phases by using approximately 0.004 normal KCl
solution. The trace amount of salt is dissolved in the aqueous phase but is
excluded from the hydrate phase. Therefore, the concentration of the salt in the
aqueous phase, measured by the electrical conductivity, gives the precise amount
of water, which goes from the liquid phase to the hydrate phase. Any electrochem-
ical reactions have to be avoided in order to make sure that the resistance mea-
surement refers only to the KCl concentration. This implies that an a.c circuit must
be used instead of a d.c. circuit since the electrodes cannot be polarized. A Gen-
rad 1689 RLC Digibridge has been used for these measurements.
B.1.3 MAGNEDRIVE STIRRER

The agitation at a constant rate is essential to recirculate the gas present in the cell, hence allows good gas-liquid surface contact. It renews the gas-liquid interfacial surface where hydrates were forming without mixing. In 1983, Vysniauskas proved that good mixing hastens the appearance of the critical hydrate nuclei. Moreover, the magnetic stirrer eliminates packing lubrication which could contaminate the sample and allow gas leakages which could occur at the packing/shaft interface. The stirrer has a pressure rating of 5,000 Psi. The belt drive is connected to the hydraulic motor that provides a stirring speed range of 0 to 300 revolutions per minute.

B.2. PRESSURE NETWORK

B.2.1 VOLUMETRIC PUMPS

The pressure system uses two vertical volumetric pumps of 500 cc each. Figure B.2 shows a side view of one of the pumps. The plungers can be run in opposite directions in order to provide a smooth continuous fluid flow, or be run independently. In fact, only the right pump was used for this experiment. Therefore, it was sometimes difficult to get a complete ramping cycle since the plungers advanced to the limit of the pump and the experiment would be prematurely terminated.
Figure B.2. Block Diagram of a Vertical Volumetric Pump

(Source: Lievois, 1987)
The limits of the pump present a major problem since the experiment has to be run within a given displacement range, which necessitates that the plungers come back to its initial position. The required modifications to use both right and left pumps would have taken too much time.

As the temperature decreases, the packing gland shrinks, requiring a tightening of the packing flange in order to maintain the seal. The pump does this automatically through its “self-compensating” design. The vertical plunger travel distance of 1 millimeter corresponds to 5 revolutions of the input shaft. This implies that 1 revolution of the input shaft will be equivalent to a volume displacement of 0.40 cubic centimeter. For a more thorough explanation, please refer to Lievois’ Thesis.

B.2.2 PUMP DRIVE EQUIPMENT

The equipment consists of two independent drive mechanisms, the synchronous motor and the stepping motor.

B.2.2.1 Synchronous Motor

This mechanism is based on a one horsepower, 1800 RPM synchronous motor coupled to a 28 speed “Quick Change” transmission. The 28 speeds translate into a range of continuous pump flow rates from 0.15 to 32 cubic centimeters/min.
The transmission is connected to each pump input shaft and allows them to move together, in opposing directions, or individually, by disengaging the drive coupling of the other pump input shaft.

B.2.2.2 Stepping Motor

The stepping motor is actuated by a digitally based driver which is controlled by the computer via the IEEE Interface card, (AT-GPIB/TNT+), purchased from National Instruments. The system consists of the stepping motor, the Digidrive 1073, a transformer, and 2100 Indexer with an IEEE 488 Interface card.

The stepping motor, one and half horse power motor, has a torque rating of 375 inch-lbs at 240 RPM. The motor resolution is 1000 steps per revolution. The flow rate ranges are from 5 to about 96 cubic centimeters/minute. The pump can be run in opposing mode, or independently, since there is no reversing transmission connected between the stepping motor and the pump input shafts. A counter, on the top of the deck, gives the displacement of the plunger, 10,000 steps corresponding to a displacement of 12 on the counter reading. Therefore, 10 revolutions correspond to 4 cubic centimeters (which is a displacement of 12 on the counter reading). By using this relationship, the computer gives the direct volumetric measurement and therefore the evolution of the volume of gas added/removed from the cell during the cooling/heating cycle.
B.2.3 TUBING AND VALVE SYSTEM

Please refer to Figure B.1 for a better understanding of the schematic of the pressure system and the different valves. In each valve, Autoclave Engineers, there are three ports. Two are always connected and the last one is valved off. They are pressure rated to 11,000 psi.

Two rupture disks (rated 5,000 psi) are placed downstream of each pump in order to prevent the gas from going to the vapor vent, which are fed out to the roof of the building.

The vacuum system consists of the vacuum pump, the vacuum manifold, the associated valves, the reservoir tank and the vacuum gauge. The reservoir tank has a volume of 40 liters which allows a "reservoir at vacuum". The pressure measurements are made by two HEISE pressure transducers, each rated for 10,000 Psi at 0.07 percent accuracy at full scale. They are directly connected at the top of the deck in order to eliminate unthermostatted pressure lines and the resulting temperature effect on the sample in the cell. They are connected to the computer via a serial interface card RS232.
B.3. TEMPERATURE CONTROL

Fine temperature control is achieved by combining cooling and heating. A large refrigeration unit is running at a fixed setting rate while a small electrical heater provides the heat necessary to provide precise temperature control at a given ramping rate. The temperature control in the bath is provided both by the heater banks, (auxiliary bath heater and bath heater), and by the refrigeration unit.

B.3.1 HEATER BANKS

The heater banks or blower section consist of sixteen coiled Nichrome heating elements that are each rated for two kilowatts.

Twelve are controlled by the computer and four are tied in series to a Variac power supply for manual operation. The twelve heating elements form four heater banks, each with three elements tied in series. They are connected to a solid state relay which is linked to a temperature controller (Model 808), furnished by Eurotherm Controls, interfaced to the computer via the serial interface card RS232. Therefore, the multiplexing system built by Lievois in 1987 has been completely removed and simplified as is shown in Figure B.3.

B.3.2 REFRIGERATION UNIT

The refrigeration unit is a single stage unit with three separate expansion valves. It can be run with Freon R12, Freon R502, or both, at the same
Figure B.3. Block Diagram of the Bath and Refrigeration Unit
time. For these experiments, only Freon 502 has been used since it was needed to achieve some cold temperatures in the bath. Dry air circulates inside the bath in order to prevent water condensation at low temperature. Pure nitrogen is preferred inside the bath since it is not combustible. The air temperature is circulated throughout the upper section of the bath via six blowers placed at the bottom of the blower section.

B.3.3 TEMPERATURE CONTROL

The temperature control in the air bath is achieved very precisely since the digital controller uses a PID algorithm and all the parameters are already configured in the controller. The controller was calibrated by EUROTHERM Controls. Thirty parameters can be modified manually for the operation of the instrument, but only the following ones are modified for each experiment: the setpoint value and the ramping rate. The other parameters are set for all of the experiments and never modified. The range of the setpoint ramping rate is from 0.01 °C/min to 99.99 °C/min. But only three ramping rates have been used, 0.01 °C/min (0.6 °C/hr), 0.02 °C/min (1.2 °C/hr) and 0.04 °C/min (2.4 °C/hr), slowly enough to provide a quasi-equilibrium state in the cell at each temperature. With 0.6 °C/hr, the experiments last 60 hours for Methane and 41 Hours for Carbon Dioxide. The temperature in the bath is measured with a 100 Ohms RTD, placed in the surrounding block and connected to the digital temperature controller.
The 500 Ohms RTD used previously by Lievois in the surrounding block could not be used since the digital controller is only configured for 100 Ohms RTD'S.

The temperatures in each cell are measured with two 500 Ohms RTD's connected to a relay, which was built at Rice University by Mr. Richard Chronister. The advantage of this relay is to use only one Keithley to measure the temperatures in both cells at the same time, by switching from one to the other. The relay is connected both to the Keithley and to the computer via a digital Input/Output card. This card provides the input to the relay whose output is transmitted to the Keithley. The Keithley, 192 programmable 6 1/2 digital multimeter, is connected to the computer via the IEEE interface card. The Keithley gives a resistance measurement which is converted to the temperature in Degree Celsius via a formula explained in the Visual Basic program, (Callendar-Van Dusen Equation). For more explanations, please refer to Figure B.4 and Appendix A. Therefore, the temperatures in the block and in the cells are controlled very precisely through three RTD's connected to the computer, (Figure B.4).
Figure B.4. Block Diagram of the Pressure and Temperature Controls and Data Logging System
B.4. COMPUTER/DATA ACQUISITION NETWORK

The performance of the calorimeter apparatus strongly depends on the control and data acquisition program for the PC. The program is written in Visual Basic and is able to set heater load and pump position (i.e. volume of gas added to or pulled from the cell during the experiment), while controlling the temperature accurately. Therefore, this program is essential for the experiments since it must handle various data acquisitions from the Genrad (Electrical Conductivity), the HP multimeter (Thermopile), the three RTD's and the HEISE pressures transducers. The data acquisition is performed every minute, while the pressure is controlled every four seconds. This allows very good control, especially for the experiments which usually last more than two days.

B.4.1 IEEE INTERFACE

The IEEE interface or AT-GPIB/TNT+ card is the heart of the computer since it handles most of the data. Purchased from NATIONAL INSTRUMENTS, the AT-GPIB/TNT+ card with a NI-488.2 software for Windows transforms a general purpose PC into a GPIB Talker/Listener/Controller that has complete communications and bus management capabilities. This board is equipped with a TNT4882C unit, which implements the HS488 high-speed control, hence increasing a maximum data transfer rate from the instruments to the computer. Simultaneously, IEEE interface card controls the stepping motor, the Genrad, the HP multimeter and the Keithley.
B.4.2 SERIAL INTERFACE

The serial interface card or RS232 is a CyberProQuad I/O card which provides four high-speed 16550 serial ports, two 9-pin and two 25-pin. This card is a 16-bit high-speed/high IRQ/multi-COM-port I/O card, purchased from SIIG. Two HEISE pressure transducers and the temperature controller are connected to the computer via this card.

B.4.3 DIGITAL I/O CARD

This digital I/O card or CIO-DAS08 is purchased from OMEGA Engineering and is able to send a digital input to the relay in order to get the two temperatures in each cell of the calorimeter at the same time. The software for this card uses the “Universal Library language”.

Therefore, through these three cards, the computer is able to handle all the data which are used in the following parts to provide very useful information on the gas solubility in the liquid phase at and “near- hydrate formation conditions”, and some of the derived thermo-physical properties such as the enthalpy or the entropy change during the phase changes taking place. Basically, the computer is essential to give a better understanding of the formation/decomposition process that takes place in the right cell of the calorimeter, as viewed in Figure B.1.
C. SOLUBILITY MEASUREMENTS

C.1 EXPERIMENTAL RESULTS

C.1.1 PRESENTATION

Information on the solubility of gases like methane or carbon dioxide in pure water is very useful to calculate the enthalpy of solution/dissociation and entropy of change of the solution. The gas solubility has been extensively studied and found to be extremely low (Culberson and Mc Ketta, 1950; Kobayashi, 1951; Katz et al., 1959; Clever et al., 1980, 1984; Battino, 1986, 1987; Fleyfel et al., 1993; Feneyrou, Song et al., 1996). This information at low temperature and high pressure is very scarce, due to the appearance of hydrate solid phase or metastable phases which make the measurements difficult. In this work, the solubility of methane, carbon dioxide, and methane (5%)-carbon dioxide has been measured at different pressures and different ramping rates, as is shown in table C.1.

At these conditions, all components, methane, carbon dioxide, and methane(5%)-carbon dioxide mixtures, are in gaseous state for a temperature range of 291 to 278 K. For the methane at 3.86 MPa, the temperature range is 288 to 273 K. This range includes the hydrate formation conditions and the measurements were made each time throughout the entire hydrate formation/decomposition cycle.
The pressure was measured with a Heise pressure transducer, rated at 10,000 Psia, and the stepping motor allowed very good control of the constant pressure. The agitation of the gas is achieved with the magnetic stirrer.

Table C.1 Isobaric Experiments with different gases

<table>
<thead>
<tr>
<th></th>
<th>Pressure (Psia)</th>
<th>Ramping Rate (° C/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>1520</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2020</td>
<td>1.2</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>0.6</td>
</tr>
<tr>
<td>Methane (5%)-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>560</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Dew point pressure for pure carbon dioxide, for low temperature at which hydrate formation occurs, was around 690 psia. The same pressure for methane, carbon dioxide, and methane-carbon dioxide mixture has been used for the purpose of direct comparison. It is essential to stay on the three-phase line Lw-H-V locus in order to avoid the formation of ice or liquid hydrocarbons that would interfere with the experiment. Figure C.1 and C.2 show this three-phase line for pure methane and methane-carbon dioxide. A ramping rate of 0.6 °C/hr has been chosen for a pressure of 560 Psia since it was the only ramping rate which allowed hydrate formation.
Figure C.1. Pressure-Temperature Diagram for the Methane-Water System

(Source: Kobayashi and Katz, 1949)
Figure C.2. Pressure-Temperature Diagram for Carbon Dioxide-Methane System

(Source: Unruh and Katz, 1949)
Several ramping rates have been tried, 1.2° C/hr, 1.8° C/hr and 2.4° C/hr but none of them showed any hydrate formation. Therefore, for low pressure, the lowest ramping rate is preferred in order to insure sufficient hydrate formation.

The limits of the pump were also a major factor in achieving a complete cycle. Therefore, it has been sometimes painstaking to obtain a cooling/heating run with the differential calorimeter since the ramping rate and the volume of the pump are two major parameters to be controlled together.

C.1.2 VOLUME-TEMPERATURE RESULTS

The results are shown in Figures C.3 to C.14. Two runs have been conducted for each pressure and each ramping rate. Each component shows very good reproducibility of the volume of gas added versus temperature or versus time for the same conditions of pressure and ramping rates. Moreover, the temperature versus time indicates very good control at the desired ramping rate.

For each study: methane, carbon dioxide, and methane (5%)-carbon dioxide mixture, the following plots are shown:

* Volume versus Temperature
  * Volume versus Time
  * Temperature versus Time
Each cycle exhibits an hysteresis, characteristic of all runs made with methane or carbon dioxide, whatever the pressure or the ramping rate. However, the hysteresis is much bigger with a faster ramping rate. From these plots, seven different regions along the cooling/heating curves are exhibited:

** COOLING

(1) An interstitial solubility where the gas is dissolved into water according to Henry’s Law.
(2) The solubility of the gas starts increasing beyond that accounted for by Henry’s Law.
(3) The gas intake by the water increases and this point being called the Catastrophic Temperature Tc. The solubility continues to increase.
(4) The catastrophic hydrate formation occurs and the amount of solid hydrate present in the water has drastically increased.
(5) The solidification starts, but the magnetic stirrer is still running. Noise in the cell indicates that hydrates are being crushed.

** HEATING

(6) The dissociation of the hydrates begins. The hydrate crystals start melting, hence the volume maintains a constant value.
(7) The volume drops very fast and the hydrates are almost completely decomposed. The volume returns close to its initial value.
Figure C.3. Change of Volume vs. Temperature for a Methane-Water System at 3.86 Mpa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.4. Change of Volume vs. Time for a Methane-Water System at 3.86 MPa (560 Psia) when the Air Bath is ramped at 0.6°C/hr.
Figure C.5. Change of Temperature vs. Time for a Methane-Water System at 3.86 MPa (560 Psia) when the Air Bath Is ramped at 0.6°C/hr
Figure C.6. Change of Volume vs. Temperature for a Methane-Water System at 10.48 MPa (1520 Psia) when the Air Bath Temperature is ramped at 1.0°C/hr.

Volume (cc) of CH₄ added at 10.48 MPa (1520 Psia)
Figure C.7. Change of Volume vs. Time for a Methane-Water system at 10.48 MPa (1520 Psia) when the Air Bath Temperature is ramped at 1.2°C/hr.
Figure C.8. Change of Volume vs. Temperature for a Methane-Water System at 13.93 MPa (2020 psia) when the Air Bath Temperature is ramped at 1.2°C/hr
Figure C.9. Change of Volume vs. Temperature for a Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr.
Figure C.10. Change of Volume vs. Time for a Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.11. Change of Temperature vs. Time for a Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.12. Change of Volume vs. Temperature for a Mixture Methane(5%)-Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath is ramped at 0.6°C/hr
Figure C.13. Change of Volume vs. Time for a Mixture Methane(5%)-Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath is ramped at 0.6°C/hr
Figure C.14. Change of Temperature vs. Time for a Mixture Methane(5%)-Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath is ramped at 0.6°C/hr
C.1.3 ELECTRICAL CONDUCTIVITY RESULTS

The method, used by Lieveois to track the water between the hydrate phase and the liquid phase, was based on monitoring the change of electrical conductivity of the liquid water phase. This phase contained a small amount of dissolved potassium chloride, about 0.002 normal. The low concentration of KCl insures that there will be no effect of the salt concentration on the hydrate properties. The conductivity measurement is made via an electrical conductivity cell located inside the calorimeter cell, at the bottom of the cell. The electrical conductivity cell must be immersed in the liquid water phase and care must be taken not to form too much hydrate in order to prevent the hydrate phase from going into the electrical conductivity cell region. As the KCl ions are excluded from the clathrates cages of the hydrate, the movement of the water molecules between the hydrate phase and the liquid phase changes the concentration of the KCl in the liquid phase. The relationship between the electrical conductivity and KCl concentration is well-understood and defined. Therefore, the determination of the KCl concentration allows a quantitative tracking of the water.

In these experiments, the amount of water in the hydrate phase was determined via solubility measurements. However, a potassium chloride solution, around 0.004 normal, was prepared and charged into the cell in order to get a better understanding of the change of the electrical conductivity versus temperature or versus time.
Pure water is known to be a poor conductor of electric current. However, the presence of ionic species, like KCl, drastically changes the conductive capabilities since they conduct the current. A conductance equation, based on Debye-Hückel theory, was first proposed by Onsager:

$$\Lambda = \Lambda_0 - (S \cdot c^{1/2})$$

where $\Lambda$ is the equivalent conductance (or conductance per moles of charges) of the solution

$\Lambda_0$ is the equivalent conductance at infinite dilution

$\Lambda$ and $\Lambda_0$ are expressed in $cm^3/\Omega.cm$ equivalents

$S$ is a function of the solvent properties

$c$ is the electrolyte concentration (equivalents/liter)

Most commonly used today is an extension of Onsager’s Equation, the Fuoss-Onsager’s Equation:

$$\Lambda = \Lambda_0 - (S \cdot c^{1/2}) + (E \cdot c \cdot \log(c)) + (J - (F \cdot \Lambda_0)) \cdot c + (J_2 \cdot c^{3/2})$$

where $S$, $E$, $J$ and $J_2$ depends on the electrophoretic and relaxation effects and on $\Lambda_0$. $J$ and $J_2$ are also function of the ion size parameter. The term $F \cdot \Lambda_0 \cdot c$ is a function of the change in bulk viscosity of the solution with addition of the electrolyte. Please refer to Lievois’s Thesis for more details.
For solutions with solvents of large dielectric constant (>30) and large ions, Fuoss, Onsager, and Skinner showed that the previous equation simplifies to:

$$\Lambda = \Lambda_0 - (S \cdot c^{1/2}) + (E \cdot c \cdot \log(c)) + J \cdot c$$

The specific conductance $C_s$ (1/Ω.cm), is related to the resistance $R$ (Ω) between the electrodes by the equation:

$$C_s = \frac{L}{R}$$

where $L$ (cm) is the so-called cell constant. The calibrations, made by Lievois, give an average value for $L$ equal to 0.316 $cm^{-1}$.

The equivalent conductance $\Lambda$ is related to the specific conductance via the equation:

$$\Lambda = \frac{1000 \cdot C_s}{c}$$

Therefore, the equivalent conductance and the concentration are related to the resistance via the equation:

$$\Lambda = \Lambda_0 - (S \cdot c^{1/2}) + (E \cdot c \cdot \log(c)) + J \cdot c = \left(\frac{1000}{c} \cdot \frac{L}{R}\right)$$
Thus, the relation between the measured resistance value $R$ and the salt concentration $c$ is:

$$\Lambda_0 \cdot c - (S \cdot c^{3/2}) + (E \cdot c^2 \cdot \log(c)) + J \cdot c^2 = 1000 \cdot \frac{L}{R}$$

From this relationship, the concentration of KCl will increase when the resistance value will decrease and vice-versa. In order to insure that the resistance measurement is only indicative of KCl concentration, any electrochemical reactions must be avoided. Therefore, the electrodes are not polarized, as is the case in D.C. (direct current) circuit resistance measurement, and an A.C. (alternating current) circuit is used. The parameters in this equation could not be determined since $\Lambda_0$ is a function of the temperature and the other parameters, $S$, $E$ and $J$, are function of $\Lambda_0$. Lievois used the simplified equation of Fuoss-Hsia since he worked at constant temperature, (all the parameters were constant). However, in isobaric mode, all parameters depend on temperature. Therefore, the measured value for $R$ in these experiments are only semi-quantitative.

The following plots, C.15 to C.20, show the change in the measured resistance value versus temperature and versus time. Signal averaging was used since the direct measurement showed a lot of fluctuations. These fluctuations would have been less important if we had used a lower sensitivity for the Genrad. However, these results are interesting since very few data are available in the literature for the electrical conductivity of different gases at constant pressure.
Figure C.15. Change of Electrical Conductivity vs. Temperature for a Methane-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.16. Change of Electrical Conductivity vs. Time for a Methane-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.17. Change of Electrical Conductivity vs. Temperature for a Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.18. Change of Electrical Conductivity vs. Time for a Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.19. Change of Electrical Conductivity vs. Temperature for a Methane(5%)-Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.20. Change of Electrical Conductivity vs. Time for a Methane(95%)-Carbon Dioxide-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Most of the previous works, especially by Lievois, were done at constant temperature. These plots exhibit seven different regions, as shown in the volume versus temperature plots:

(1)-(3) The measured resistance value increases until the catastrophic point $T_c$ is reached. For each component, the slope is straight and no fluctuations are observed.

(4) Just after $T_c$, the amount of hydrate solid has increased. Several fluctuations are observed, due to the formation of hydrate gas. However, it might be due also to the noise in the calorimeter system which creates these irregularities. The slope is no longer straight, but the resistance still increases, usually showing a decrease in the salt concentration. However, as soon as the hydrate starts forming, the salt concentration should increase, since salt is excluded from the hydrate phase. This has been verified at constant temperature. However, since all the parameters, $A_0$, $S$, $E$ and $J$, depend on the temperature, pressure, and ion size parameter, it seems that these parameters have an effect more important than the salt concentration on the resistance values read. These parameters decrease more than the salt concentration increases, hence increasing the resistance value.

(5) However, as hydrate solid phase aggregates, a sudden decrease in the resistance value is observed. This verifies that the concentration of KCl increases as hydrate formation increases, since salt is excluded from the hydrate phase.
The heating starts and the parameters increase, as temperature increases. Therefore, both parameters and concentration increase, hence decreasing the resistance value.

(6) As the dissociation of the hydrates begins, the hydrate crystals start melting, hence the measured resistance does not change. The salt concentration maintains a constant value as the volume added in the cell. Please refer to plots C.3 to C.14.

(7) The volume drops very fast and the hydrates are almost completely decomposed. Therefore, the salt concentration should decrease since the amount of free water increases. This has been verified by the measured resistance values which increase very fast, on complete decomposition of hydrate crystals. The salt concentration decreases more than the increase of the parameters.

Therefore, several similarities have been found between: Volume-Temperature and Resistance-Temperature, Volume-Time and Resistance-Time. Moreover, several conclusions are drawn from these results. Until $T_c$ and just after, (1-4), the gas hydrates start forming and the salt concentration increases. However, the parameters, $\Lambda_0$, S, E and J, decrease more with decreasing temperature than the salt concentration increases, hence increasing the resistance value. However, as soon as hydrate formation begins to increase much faster, (5), the salt concentration seems to follow the change in the hydrate phase, i.e. increasing when the hydrate phase increases and decreasing when the hydrate is
almost decomposed, (7), hence releasing free water to the liquid phase. Therefore, in the isobaric mode, temperature-ramping, the resistance value depends not only of the concentration, as is the case for isothermal experiments, but also on the temperature.

C.1.4 THERMOPILE RESULTS

The thermopile readings give the temperature difference between the cell and the surrounding block. This signal is read with the HP multimeter, connected to the computer via the IEEE interface. Lieveos used a calibration factor $K$ that relates the heat flux to the thermopile signal:

$$ K = \frac{Q}{\sum (mV - min)} $$

Where $Q$ is the heat generated or consumed in the cell (calories).

$\sum (mV - min)$ is the area under the response curve Thermopile-Time.

$K$ is function of the temperature. Since he worked at constant temperature, $K$ was constant. However, in temperature-ramping mode, this coefficient is no more constant and the calculations of the heat of dissociation is much more difficult. Moreover, the readings are very sensitive and the noise gave some big fluctuations on the plots. Even by using signal averaging, the thermopile reading is not precise enough to get any information. Please refer to Lieveos’s Thesis (Chapter 4) for more details.
Figures C.21 and C.22 give the change of thermopile values versus time for pure methane and methane(5%)-carbon dioxide mixture at 560 Psia and a ramping rate of 0.6 °C/hr. A comparison is made with the change of temperature versus time, for the same conditions of pressure and ramping rate.

The results seem consistent since the thermopile signal increases until the end of the cooling part in the bath, then decreases until the end of the heating part. When the temperature starts increasing in the bath, the temperature still decreases in the cell, around 1 or 2 °C. Therefore, the maximum of the cooling part in the cell does not correspond exactly to the maximum of the thermopile signal.

Even if these results are consistent with the cooling/heating process, no direct heat of dissociation could be calculated. Therefore, the enthalpies of solution and dissociation were calculated via solubility measurements and the use of the Clausius-Clapeyron Equation. Please refer to part D for more details.
Figure C.21. Change of Thermopile Signal and Temperature vs. Time for a Methane-Water System at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
Figure C.22. Change of Thermopile Signal and Temperature vs. Time for a Methane(5%)-Carbon Dioxide-Water Mixture at 3.86 MPa (560 Psia) when the Air Bath Temperature is ramped at 0.6°C/hr
C.2 DATA ANALYSIS AND DISCUSSION

C.2.1 CATASTROPHIC AND FINAL HYDRATE DECOMPOSITION TEMPERATURES

For each component, the catastrophic temperature, $T_c$, and the final hydrate decomposition temperature, FHDT, are determined by graphical interpolations. $T_c$ corresponds to the beginning of hydrate formation which shows a sudden change in the slope with increase of the solubility. FHDT corresponds to the decomposition of the last hydrate crystal, which shows a sudden decrease in solubility. The experiments have been performed at several ramping rates and it appears that the ramping rate has no effect on $T_c$ or FHDT, showing good mixing of the gas and liquid phases. The experimental values of $T_c$ and FHDT and the mean deviations with the CSMHYD temperature prediction (see Appendix C) are given in Tables C.2 to C.5. The predicted temperatures for hydrate decomposition are higher than the experimental values for each component but they are only an estimate, since they are based on the statistical thermodynamic theory of van der Waals and Platteuuw and on the correlation of empirical data, obtained from P-T measurements. Appendix C provides an overview of their theory.

Concerning pure methane, $T_c$ is more difficult to determine accurately at “low” pressure (1520 Psia) than at “high” pressure (2020 Psia).
For a pressure of 1520 Psia, the slope of the volume versus temperature at T=T_c does not change drastically. Moreover, there is no way to observe the beginning of formation of hydrates with the calorimeter, as is the case with a visual cell. Therefore, the value read for T_c might include some imperfections at "low" pressure. However, for P=560 Psia, a break is observed as soon as the hydrate starts forming. Therefore, the slowest ramping rate seems to be the more accurate method to determine T_c since the ramping rate was 0.6° C/hr for P=560 Psia, and 1.2° C/hr for P=1520 Psia. Moreover, the pure methane does not seem to give good reliability as these predictions for "low" pressures (P=560 and 1520 Psia) since the deviation may be as much as 2.8° C with an average value of 2.5° C for 1520 Psia. On the contrary, for a pressure of 2020 Psia, the predictions are much closer to the experimental values, since the average deviation is only 1.25° C.

As regard to pure carbon dioxide, the prediction for FHDT is very close to the experimental value since the deviation is only 0.25° C. This can be explained by the fact that the ramping rate (0.6° C/hr) was slow enough to provide good mixing via the magnetic stirrer, in order to insure hydrate formation. Therefore, the predictions are reliable for pure carbon dioxide. However, T_c was rather difficult to determine since there is no real break in the slope. The experiments showed that the carbon dioxide hydrates were much more difficult to detect than hydrocarbons hydrates.
Table C.2. Catastrophic and Final Hydrate Decomposition Temperature for Methane-Water system

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>560</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramping Rate (° C/hr)</td>
<td>Run#1</td>
<td>Run#2</td>
</tr>
<tr>
<td>Tc</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>FHDT</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>FHDT*</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>IFHDT*-FHDTI</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>IFHDT-Tcl</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>IFHDT*-Tcl</td>
<td>1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>1520</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramping Rate (° C/hr)</td>
<td>1.2</td>
</tr>
<tr>
<td>Run#1</td>
<td>Run#2</td>
</tr>
<tr>
<td>Tc</td>
<td>11.6</td>
</tr>
<tr>
<td>FHDT</td>
<td>16.0</td>
</tr>
<tr>
<td>FHDT*</td>
<td>13.8</td>
</tr>
<tr>
<td>IFHDT*-FHDTI</td>
<td>2.4</td>
</tr>
<tr>
<td>IFHDT-Tcl</td>
<td>4.4</td>
</tr>
<tr>
<td>IFHDT*-Tcl</td>
<td>2.2</td>
</tr>
</tbody>
</table>

FHDT* corresponds to the CSMHYD prediction, given by the Colorado School of Mines. (Sloan, 1990).
Table C.3. Catastrophic and Final Hydrate Decomposition Temperature for Methane-Water system

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramping Rate (°C/hr)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Run#1</td>
</tr>
<tr>
<td>Tc</td>
<td>14.6</td>
</tr>
<tr>
<td>FHDT</td>
<td>18.0</td>
</tr>
<tr>
<td>FHDT*</td>
<td>16.24</td>
</tr>
<tr>
<td>IFHDT*-FHDTl</td>
<td>1.76</td>
</tr>
<tr>
<td>IFHDT-Tcl</td>
<td>3.40</td>
</tr>
<tr>
<td>IFHDT*-Tcl</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Table C.4. Catastrophic and Final Hydrate Decomposition Temperature for Carbon Dioxide-Water Sytem

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>560</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramping Rate (°C/hr)</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Run#1</td>
</tr>
<tr>
<td>Tc</td>
<td>8.20</td>
</tr>
<tr>
<td>FHDT</td>
<td>9.50</td>
</tr>
<tr>
<td>FHDT*</td>
<td>9.25</td>
</tr>
<tr>
<td>IFHDT*-FHDTl</td>
<td>0.25</td>
</tr>
<tr>
<td>IFHDT-Tcl</td>
<td>1.30</td>
</tr>
<tr>
<td>IFHDT*-Tcl</td>
<td>1.05</td>
</tr>
</tbody>
</table>

FHDT* corresponds to the CSMHYD prediction. Sloan, 1990.
Table C.5. Catastrophic and Final Hydrate Decomposition Temperature for Methane(5%)-Carbon Dioxide-Water system

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>560</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramping Rate (°C/hr)</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Run#1</th>
<th>Run#2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>FHDT</td>
<td>9.45</td>
<td>9.5</td>
</tr>
<tr>
<td>FHDT*</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>IFHDT*-FHDTI</td>
<td>0.45</td>
<td>0.5</td>
</tr>
<tr>
<td>IFHDT-Tcl</td>
<td>1.25</td>
<td>1.3</td>
</tr>
<tr>
<td>IFHDT*-Tcl</td>
<td>0.80</td>
<td>0.8</td>
</tr>
</tbody>
</table>

For the mixture: methane(5%)-carbon dioxide, the same slow ramping rate, (0.6° C/hr), has been used and the predictions are also verified since the deviation is only 0.5 °C from the experimental values. The determination of $T_c$ was also rather difficult since the change of the slope was not obvious.

Therefore, the slowest ramping rate, (0.6° C/hr), gives the most accurate determination of $T_c$ and provides a closer agreement with the predictions (CSMHYD). However, further studies on a larger range of pressure and ramping rate, especially by using spectroscopy, are needed to evaluate the reliability of these predictions.
C.2.2 DETERMINATION OF SYSTEM VOLUME

The knowledge of the exact system volume is necessary for the mass balances and for computing the solubility of gases in liquid water. In using the same differential calorimeter as Lievois, the system volume was computed by loading an arbitrary amount of methane gas. Once the thermal equilibrium was reached at a given temperature T, the system volume was changed using the volumetric pump, and the pressure change was precisely recorded. The calibrated volumes determined by Lievois are given in table C.6.

The total volume does not include the left cell and the left pump since they were not used. The volumes of water and gas in the cell, which have been used for the experiments, are given in table C.7.

Table C.6. Calibrated volumes in the Calorimeter

<table>
<thead>
<tr>
<th></th>
<th>Volume (Liters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump Cylinder</td>
<td>0.659 ± 0.003</td>
</tr>
<tr>
<td>Calorimeter Cell</td>
<td>1.130 ± 0.006</td>
</tr>
<tr>
<td>Total volume</td>
<td>1.789 ± 0.006</td>
</tr>
</tbody>
</table>

The volume of water has been reduced from 650 cubic centimeters to 500 cubic centimeters in order to increase the gas volume and hence the hydrate formation.
Table C.7. Volume of Water and Gas used for each Component

<table>
<thead>
<tr>
<th></th>
<th>Pressure (Psia)</th>
<th>Water Volume (cc)</th>
<th>Gas Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>2020</td>
<td>650</td>
<td>480</td>
</tr>
<tr>
<td>Methane</td>
<td>1520</td>
<td>650</td>
<td>480</td>
</tr>
<tr>
<td>Methane</td>
<td>560</td>
<td>500</td>
<td>630</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>560</td>
<td>500</td>
<td>630</td>
</tr>
<tr>
<td>Methane (5%)-</td>
<td>560</td>
<td>500</td>
<td>630</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C.2.3 MASS BALANCES

In the isobaric mode, as the temperature is lowered, the pump adds a proportional number of moles to the gas phase for a given change of volume in the gas phase. Therefore, the solubility in the liquid phase at a given temperature $T_i$ will be the net difference between what is added to the system at $T_i$ due to gas compression and what is initially in the system at $T_0$. A rigorous mass balance has been derived in order to get the solubility of hydrate gases in the liquid phase. These experiments involve only one hydrocarbon and water. Therefore, there are two phases before hydrate formation.

Let $n_I^J$ the net amount of moles of I (Hydrocarbon or Water) in the J phase (Liquid, Vapor or Hydrate).
Two mass balances have to be derived, one on the water-rich and one on the hydrocarbon-rich phase.

* Mass balance on the water

In the system, Bath-Pump-Cell, only pure hydrocarbon gases are exchanged. Therefore, assuming that the saturation is reached, the amount of water introduced in the cell does not change between a given state 1 and a given state 2: 

\[ (n_{W}^{Cell})_1 = (n_{W}^{Cell})_2 \]

Therefore, 

\[ (n_{W}^V + n_{W}^L + n_{W}^H)_1 = (n_{W}^V + n_{W}^L + n_{W}^H)_2 \]

Assuming that the amount of water in the vapor phase does not change between the state 1 and the state 2, we end up with the following equation: 

\[ (n_{W}^L + n_{W}^H)_1 = (n_{W}^L + n_{W}^H)_2. \]

If state 1 is taken before \( T_c \) and state 2 after \( T_c \), no hydrates are present in state 1 and the equation becomes: 

\[ (n_{W}^L)_1 = (n_{W}^L + n_{W}^H)_2. \]

Therefore, the volume of gas in the cell is assumed to be constant (Volume = 480 cc or 630 cc). An example for methane is given in Appendix B.
* Mass balance on the gas

The number of moles of gas $n_{Gas}^{\text{exch}}$ exchanged between the pump and the cell is given by:

$$n_{Gas}^{\text{exch}} = ((n_G^V + n_G^L + n_G^H)_2 - (n_G^V + n_G^L + n_G^H)_1)$$

The total number of moles of gas in the cell and in the pump at a given temperature $T_i$ are computed with the following equations:

$$(n_{Gas}^{\text{Cell}})_i = (\rho_{\text{Cell}} \cdot V_{Gas}^{\text{Cell}})_i$$

$$(n_{Gas}^{\text{Pump}})_i = (\rho_{\text{Pump}} \cdot (V_{Gas}^{\text{Pump}} - V_{\text{Added Cell}})_{Gas})_i$$

$$(n_{Gas}^{\text{Total}})_i = (n_{Gas}^{\text{Cell}})_i + (n_{Gas}^{\text{Pump}})_i$$

The amount of gas added to the liquid phase, at the temperature $T_i$, is equal to the difference between the total number of moles of gas in the system at the initial temperature $T_0$ and at the temperature $T_i$:

$$(n_{Gas}^{\text{Liquid}})_i = (n_{Gas}^{\text{Liquid}})_0 + (n_{Gas}^{\text{Net}})_i$$
In order to get \((n_{Liquid})_{0}\), an extrapolation has been made from the available literature data of methane solubility (Kobayashi, 1951 - Culberson and McKetta, 1951) and carbon dioxide solubility (Wiebe and Gaddy, 1941 - Dodds et al., 1956) in water far above the hydrate formation conditions. Therefore, a reference has been established for the solubility of these two gases in pure water in the low temperature region.

Then, the solubility (or mole fraction) is obtained by the following relation:

\[
x_i = \frac{(n_{Liquid})_i}{\frac{(n_{Liquid})_i}{(n_{Gas})_i + (n_{Water})}} + \frac{(n_{Total})}{(n_{Liquid})_i}
\]

An example of calculation is given for the methane in Appendix B. In the following part, the results of the solubility of pure components, methane and carbon dioxide, in water are presented.
C.2.4 SOLUBILITY RESULTS

Table C.8 gives the values reported for methane at P=1520 Psia and P=2020 Psia. These values show the extent of divergence or increase in the solubility of methane with the baseline, obtained from the values of Culberson and McKetta.

Table C.8. Solubility of Methane Gas in Water - Temperature -Ramping Ramping Rate= 1.2 °C/hr

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>1520</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (°C)</td>
<td>11.6</td>
<td>14.6</td>
</tr>
<tr>
<td>FHDT (°C)</td>
<td>16.0</td>
<td>18.0</td>
</tr>
<tr>
<td>FHDT* (°C)</td>
<td>13.8</td>
<td>16.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>XCH4 *1000</th>
<th>Temp. (°C)</th>
<th>XCH4 *1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.0</td>
<td>2.04</td>
<td>19.0</td>
<td>2.96</td>
</tr>
<tr>
<td>16.0</td>
<td>2.41</td>
<td>17.0</td>
<td>3.22</td>
</tr>
<tr>
<td>15.0</td>
<td>2.61</td>
<td>16.0</td>
<td>3.92</td>
</tr>
<tr>
<td>12.0</td>
<td>3.62</td>
<td>15.5</td>
<td>4.23</td>
</tr>
<tr>
<td>11.6</td>
<td>4.09</td>
<td>14.6</td>
<td>5.03</td>
</tr>
<tr>
<td>11.0</td>
<td>4.45</td>
<td>14.0</td>
<td>6.68</td>
</tr>
<tr>
<td>10.0</td>
<td>5.17</td>
<td>13.0</td>
<td>11.29</td>
</tr>
<tr>
<td>9.0</td>
<td>5.92</td>
<td>12.0</td>
<td>16.72</td>
</tr>
<tr>
<td>7.0</td>
<td>7.54</td>
<td>10.0</td>
<td>25.70</td>
</tr>
<tr>
<td>6.0</td>
<td>9.17</td>
<td>7.0</td>
<td>37.20</td>
</tr>
<tr>
<td>5.0</td>
<td>11.41</td>
<td>6.0</td>
<td>44.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2</td>
<td>52.44</td>
</tr>
</tbody>
</table>

Obtained from Culberson-McKetta

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>XCH4 *1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>1.98</td>
</tr>
<tr>
<td>25.0</td>
<td>2.62</td>
</tr>
</tbody>
</table>

FHDT* is obtained from the prediction CSMHYD (Hydrate Program of the Colorado School of Mines)
Figure C.23: Solubility (Mole Fraction) of Methane in the Water Phase vs. Temperature at 3.86 MPa (560 psia)
Figure C.24. Comparison with the Literature of the Solubility (Mole Fraction) of Methane in the Water Phase vs. Temperature at 3.86 MPa (560 Psia)
Figure C.25. Solubility (Mole Fraction) of Methane in the Water Phase vs. Temperature at 10.48 MPa (1520 Psia)
Figure C.26. Solubility (Mole Fraction) of Carbon Dioxide in the Water phase vs. Temperature at 3.86 MPa (560 Psia)

Temperature, °C

0 5 10 15 20 25 30 35 40 45 50

CO₂ mole fraction

Heating

FHDT (9.5°C)

Cooling

Catast. Temp. (To=8.2°C)
Figure C.27. Comparison with the Literature of the Solubility (Mole Fraction) of Carbon Dioxide in the Water Phase vs. Temperature at 3.86 MPa (560 Psia)
Figures C.21 to C.25 show the plots of the solubility versus temperature. Their shape differs slightly from the previous plots, Volume-Temperature, but the same characteristics are observed. It has been a common practice to determine the solubility from Henry's Law. However, this law is not followed, as shown on the plots and discussed in the following part. These plots demonstrate a sudden increase of the gas solubility from the extrapolated values. The methane gas solubility values have been compared with the values from Culberson and McKetta and the carbon dioxide solubility values with those of Dodds et al.

C.2.5 DISCUSSION

Concerning the methane gas or carbon dioxide gas, the solubility increases as the temperature is lowered and a large departure from Henry's Law is observed. Therefore, Henry's Law is only applicable over a restricted range for dilute solutions and, in practice, is only a limiting law. A slight divergence to Henry's Law starts below 17.0°C for the methane gas, showing that the liquid solution becomes supersaturated with methane gas, and below 15°C for the carbon dioxide gas. Song et al. attributed this increase to a “sorption” effect with the ordering of water molecules into an ice-like structure with the water molecules surrounding the hydrocarbon molecules. This phenomena is found to occur at temperatures even higher than the catastrophic temperature $T_c$. In fact, it occurs around 15 or 16°C, which is far from the catastrophic temperature.
According to several authors, Pauling (1959), Frank and Wen (1957), Klotz (1960) and Fujihara (1968) and more recently Song et al. (1995), the water molecules in the liquid state could be considered as short-lived clusters linked together by hydrogen bonds.

The clusters are continually breaking and forming with the whole system in dynamic equilibrium (or metastable equilibrium). These ordered structures result from the contact of the hydrocarbon with water which induces small dipole moments into the hydrocarbon molecules and allows some ordering through weak dipole-induced-dipole interactions with the water. The number of water molecules affected by the interaction with the hydrocarbon solute is related directly to the size of the guest molecule, i.e., the contact surface of the guest molecule. Therefore, the size of the “ice-like” structures will increase with the size of the hydrocarbons dissolved there in.

At $T_c$, the catastrophic temperature at which hydrate crystals start to form, the methane gas solubility is increased by 192% for 560 Psia, 75% for 1520 Psia and 51% for 2020 Psia. The comparison was made with the experimental values of Culberson and McKetta (1950). The carbon dioxide solubility is increased by 29% at 560 Psia. The values by Dodds et al. (1956) were chosen as reference values. Just before and after $T_c$ (the hydrate crystals are formed), the solubility still increases, showing a high level of supersaturation of methane gas in the liquid water. These solubility measurements emphasize a crystallization-like process, which takes place during the hydrate formation.
The dissolved gas molecules form the nuclei which initiate the process of hydrate precipitation and crystal growth. One might assume that around $T_c$, the nucleation occurs as a result of a fluctuation in free energy due to the local temperature and pressure fluctuations, which are of sufficient magnitude to surmount the free energy barrier.

Therefore, the increased solubility is due to two factors: the normal van der Waals forces dispersing the molecules randomly in the water and the clustering of the water molecules providing the "dissolved structure", resulting in a somewhat milky "solution". Thus, the water molecular clustering itself provide the enhanced solubility. In 1988, Holder and co-workers studied the thermodynamic solubility of methane around the hydrate formation point. They found that, for equilibrium conditions, the solubility was not enhanced beyond the values given by Culberson and McKetta. At the same time, Englezos et al. determined that the methane concentration appeared to be supersaturated in the solution as a function of time prior to the secondary nucleation, which was called the hydrate nucleation or turbidity point. Therefore, the end of the period of increased solubility is the time when the critical nucleus size is determined, the time when the secondary nucleation begins. A more "in depth" explanation of the kinetics is given in the part F. It seems that the most likely place for the crystals to grow is located at the point of contact of the crystal-water interface, where the concentrations of gas are the highest.
After formation and decomposition, the solubility almost comes back to its initial value (Refer to Figures C.21 and C.24). This ensures that good mixing was achieved in the cell. Moreover, the comparison of the hysteresis between methane and carbon dioxide gas solubility shows that the cycle is much larger for methane gas than for carbon dioxide gas.

For methane, a larger ramping rate gives a larger hysteresis and $T_c$ appears to be less obvious on the plot, as is discussed in the part C.2.1. A big increase in solubility indicates that many hydrate cages are stabilized and assembled together, hence requiring more hydrocarbon solute molecules to participate.

The experimental data on the solubility of the mixture methane-carbon dioxide are quite limited. Several studies have been done: Unruh and Katz in 1949, Berecz and Balla-Achs in 1983 and Adisasmito in 1991. Song, in 1991, determined the solubility for this mixture using a gas chromatograph. Unruh and Katz explained that the process of formation for methane-carbon dioxide hydrate is much slower than for pure carbon dioxide. The plots C.9 and C.12 do not show a big difference between the hydrate formation of pure carbon dioxide and the mixture since the mixture is only 5% methane. These authors worked with 46.1 to 17.6% methane in the mixture of methane and carbon dioxide. Moreover, the methane composition, less than 12%, was chosen in order to avoid the coexistence of three phases to occur.
Berecz and Balla-Achs drew the attention to a “retrograde condensation” which may occur during the hydrate formation and hence change the conditions of hydrate formation and decomposition. Care was taken to avoid any non aqueous liquid phase during the hydrate formation process. Moreover, the hydrates, rich in carbon dioxide and containing a small amount of methane, have a very “loose structure”, especially in the presence of inhibitors like methanol. Further studies should include inhibitors on this mixture.

From this study, it appears that, even far from the catastrophic temperature, the gas solubility starts increasing much faster than the predicted values calculated by Henry’s Law or the literature values from Culberson and McKetta or Dodds et al. The calculated solubilities for pure components have been used to determine the enthalpies of change, dissolution and dissociation, and entropy change of methane and carbon dioxide.
D. ENTHALPY AND ENTROPY CHANGE

D.1 EXPERIMENTAL RESULTS

D.1.1 PRESENTATION

The information on the enthalpy of solution, enthalpy of dissociation and entropy changes are essential to have a better understanding of the hydrate formation/dissociation phenomena. Moreover, these derived thermo-physical properties give very useful information on the hydrate structures.

At each temperature, the equilibrium is assumed to be reached. Therefore, the enthalpy of solution can be expressed with the following relation:

\[
\left( \frac{\partial (\ln x_i)}{\partial \left( \frac{1}{T} \right)} \right)_{P, \text{sat}} = - \frac{(H_i^0)_L - (H_i^{\text{ideal}})_G}{R} = - \frac{\Delta \bar{H}_i}{R}
\]

where \((\bar{H}_i^0)_L\) is the partial molal enthalpy of the solute gas in the standard state of an infinitely dilute solution.

\((\bar{H}_i^{\text{ideal}})_G\) is the partial molal enthalpy of the ideal gas in the vapor phase.

\(x_i\) is the solubility of the pure component (CH₄ or CO₂).
The quantity \((\overline{H}_i^0)_L - (\overline{H}_i^{ideal})_G\) represents the partial molal heat of solution based on the standard state referred to infinite dilution. The heat of formation was calculated using the same expression. However, Himmelblau, in 1959, noted that this extrapolation is improper since the gas solubility increases so fast around the catastrophic temperature \(T_c\) that the basic assumptions concerning the ideal dilute solution no longer apply.

The entropy change, assuming that equilibrium is reached, is given by the relation:

\[
\left( \frac{\partial (\ln x_i)}{\partial (\ln T)} \right)_{P, \text{sat}} = \frac{(S_i^0)_L - (S_i^{ideal})_G}{R} = \frac{\Delta S_i}{R}
\]

where the quantity \((S_i^0)_L - (S_i^{ideal})_G\) represents the partial molal entropy change during the solution. The standard state used is a solution above which the fugacity of the solute gas is low enough to behave ideally.

D.1.2 Results

The plots of \(\ln(x_i)\) versus \((1/T)\) and \(\ln(x_i)\) versus \(\ln(1/T)\) are shown on the figures D.1 to D.4. The components chosen are the pure methane and pure carbon dioxide, both at the same pressure \(P=560\) Psia and the same ramping rate \(r=0.6^\circ\text{C/hr} \).
The pure methane has been compared with the values given by Culberson and McKetta (1950) and the pure carbon dioxide with the values given by Dodds et al. (1956).

The enthalpies and entropies change have been calculated at four different ranges of temperature where an approximately straight line was observed each time. Therefore, over these ranges, the enthalpies and entropies are constants. The values obtained are given for each component, pure methane and pure carbon dioxide, with different ramping rates, in the tables D.1 to D.5.

The four regions, given in each table, are the following ones:

** Before hydrate formation: Far from $T_c$, just before $T_c$.

** After hydrate formation: Just after $T_c$, far from $T_c$.

For each component, the enthalpies and entropies change are negative, which is in agreement with the literature (Himmelblau, 1959; Rettich et al., 1981; Lievois, 1987; Song and Feneyrou, 1996). A comparison with the literature is given in the following section.
Figure D.1. Logarithm of Solubility (Mole Fraction) of Methane in the Water Phase vs. Reciprocal of the Absolute Temperature at 3.86 MPa (560 Psia)
Figure D.2. Logarithm of Solubility (Mole Fraction) of Methane in the Water Phase vs. Logarithm of Absolute Temperature at 3.86 MPa (560 Psia)
Figure D.3. Logarithm of Solubility (Mole Fraction) of Carbon Dioxide in the Water Phase vs. Reciprocal of the Absolute Temperature at 3.86 MPa (560 Psia)
Figure D.4. Logarithm of Solubility (Mole Fraction) of Carbon Dioxide in the Water Phase vs. Logarithm of Absolute Temperature at 3.86 MPa (560 Psia)
Table D.1. Derived Thermo-Physical Properties: Enthalpy and Entropy Change of a Methane-Water System with P=3.86 MPa (560 Psia)

<table>
<thead>
<tr>
<th>Range of temperature, °C</th>
<th>ΔH, Kcal/mole of gas</th>
<th>ΔS, Cal/mole.°K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ramping Rate=0.6 °C/hr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run#1 (T_c=3.0 °C, FHTD=5.6 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0 to 4.0</td>
<td>-11.52</td>
<td>-41.09</td>
</tr>
<tr>
<td>4.0 to 3.0</td>
<td>-11.91</td>
<td>-41.83</td>
</tr>
<tr>
<td>3.0 to 2.5</td>
<td>-67.59</td>
<td>-247.82</td>
</tr>
<tr>
<td>2.5 to 0.5</td>
<td>-43.00</td>
<td>-156.10</td>
</tr>
<tr>
<td>Run#2 (T_c=2.9 °C, FHTD=5.6 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0 to 4.0</td>
<td>-11.31</td>
<td>- 40.66</td>
</tr>
<tr>
<td>4.0 to 2.9</td>
<td>-16.74</td>
<td>- 59.86</td>
</tr>
<tr>
<td>2.9 to 2.0</td>
<td>-46.12</td>
<td>-166.31</td>
</tr>
<tr>
<td>2.5 to 0.5</td>
<td>-36.92</td>
<td>-133.60</td>
</tr>
</tbody>
</table>
Table D.2. Derived Thermo-Physical Properties: Enthalpy and Entropy Change, of a Methane-Water System with $P=10.48$ MPa (1520 Psia)

<table>
<thead>
<tr>
<th>Range of temperature, °C</th>
<th>$\Delta H$, Kcal/mole of gas</th>
<th>$\Delta S$, Cal/mole. °K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ramping Rate=1.2 °C/hr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run#1 ($T_c=11.6$ °C  FHTD=16.0 °C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0 to 12.0</td>
<td>-16.81</td>
<td>58.64</td>
</tr>
<tr>
<td>12.0 to 11.6</td>
<td>-47.73</td>
<td>-170.47</td>
</tr>
<tr>
<td>11.6 to 7.0</td>
<td>-21.13</td>
<td>74.68</td>
</tr>
<tr>
<td>7.0 to 5.0</td>
<td>-32.02</td>
<td>-115.90</td>
</tr>
<tr>
<td><strong>Run#2 ($T_c=12.0$ °C  FHTD=16.0 °C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0 to 12.5</td>
<td>-17.81</td>
<td>62.40</td>
</tr>
<tr>
<td>12.5 to 12.0</td>
<td>-42.09</td>
<td>-142.62</td>
</tr>
<tr>
<td>12.0 to 10.0</td>
<td>-36.53</td>
<td>-129.41</td>
</tr>
<tr>
<td>10.0 to 6.0</td>
<td>-20.68</td>
<td>73.19</td>
</tr>
</tbody>
</table>
Table D.3. Derived Thermo-Physical Properties: Enthalpy and Entropy Change of a Methane-Water System with P=10.48 MPa (1520 Psia)

<table>
<thead>
<tr>
<th>Range of temperature, °C</th>
<th>ΔH, Kcal/mole of gas</th>
<th>ΔS, Cal/mole.°K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ramping Rate=2.4 °C/hr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run#1 (T_c=12.0 °C</td>
<td>FHDT=16.6 °C)</td>
<td></td>
</tr>
<tr>
<td>19.0 to 14.0</td>
<td>- 0.55</td>
<td>- 1.91</td>
</tr>
<tr>
<td>14.0 to 12.0</td>
<td>- 4.49</td>
<td>- 15.64</td>
</tr>
<tr>
<td>12.0 to 11.0</td>
<td>- 68.25</td>
<td>-241.79</td>
</tr>
<tr>
<td>11.0 to 4.0</td>
<td>-27.68</td>
<td>- 98.84</td>
</tr>
<tr>
<td>Run#2 (T_c=12.0 °C</td>
<td>FHDT=16.2 °C)</td>
<td></td>
</tr>
<tr>
<td>19.0 to 13.5</td>
<td>- 2.55</td>
<td>- 8.83</td>
</tr>
<tr>
<td>13.5 to 12.0</td>
<td>- 18.65</td>
<td>- 64.41</td>
</tr>
<tr>
<td>12.0 to 11.8</td>
<td>- 97.92</td>
<td>-349.71</td>
</tr>
<tr>
<td>10.0 to 5.0</td>
<td>-21.47</td>
<td>- 76.60</td>
</tr>
</tbody>
</table>
### Table D.4. Derived Thermo-Physical Properties: Enthalpy and Entropy Change of a Methane-Water System with $P=13.93$ MPa (2020 Psia)

<table>
<thead>
<tr>
<th>Range of temperature, °C</th>
<th>$\Delta H$, Kcal/mole of gas</th>
<th>$\Delta S$, Cal/mole.$^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ramping Rate=1.2 °C/hr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run#1</strong> ($T_c=14.6$ °C  FHDT=18.0 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.0 to 17.0</td>
<td>- 7.12</td>
<td>- 24.36</td>
</tr>
<tr>
<td>16.0 to 14.6</td>
<td>-27.51</td>
<td>- 95.23</td>
</tr>
<tr>
<td>14.6 to 13.0</td>
<td>-87.76</td>
<td>-308.86</td>
</tr>
<tr>
<td>12.0 to 6.0</td>
<td>-26.07</td>
<td>- 92.28</td>
</tr>
<tr>
<td><strong>Run#2</strong> ($T_c=14.2$ °C  FHDT=17.0 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.0 to 15.0</td>
<td>- 1.04</td>
<td>- 3.59</td>
</tr>
<tr>
<td>15.0 to 14.2</td>
<td>-65.26</td>
<td>-226.09</td>
</tr>
<tr>
<td>14.2 to 13.5</td>
<td>-168.26</td>
<td>-595.93</td>
</tr>
<tr>
<td>12.0 to 8.0</td>
<td>- 25.98</td>
<td>- 91.94</td>
</tr>
</tbody>
</table>
Table D.5. Derived Thermo-Physical Properties: Enthalpy and Entropy Change of a Carbon Dioxide-Water System with \( P = 3.86 \) MPa (560 Psia)

<table>
<thead>
<tr>
<th>Range of temperature, °C</th>
<th>( \Delta H ), Kcal/mole of gas</th>
<th>( \Delta S ), Cal/mole.°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ramping Rate=0.6 °C/hr</td>
<td></td>
</tr>
<tr>
<td>Run#1 (Tc=8.2 °C) FHDT=9.5 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.4 to 11.0</td>
<td>- 7.10</td>
<td>-24.79</td>
</tr>
<tr>
<td>10.0 to 8.2</td>
<td>- 9.84</td>
<td>-34.74</td>
</tr>
<tr>
<td>8.2 to 8.0</td>
<td>- 22.10</td>
<td>-78.91</td>
</tr>
</tbody>
</table>

D.2 DATA ANALYSIS AND DISCUSSION

D.2.1 Enthalpy of Solution

Figures D.5 and D.6 give the enthalpies of solution for pure methane gas and pure carbon dioxide gas in water. A comparison with the literature, at different pressures, show a reliability of the results obtained in this work since the enthalpy of solution for methane gas increases with the increasing pressure as predicted. From the atmospheric pressure to 137 Atm (2020 Psia), the enthalpy of solution increases from -4 Kcal/mole of gas at 15°C to -28 Kcal/mole of gas at the same temperature.
Figure D.5. Enthalpies of Solution for Pure Methane
Figure D.6. Enthalpies of solution for Pure Carbon Dioxide
Concerning the carbon dioxide at 560 Psia, the scarcity of the literature values does not allow a check of these results. The only results found are these from Feneyrou, obtained at 500 Psia (34 Atm). At the temperature of T=10°C, almost the same value is obtained. Therefore, the values for the enthalpy of solution for methane and carbon dioxide gas appear to be consistent with the literature.

Table D.6. Standard Molar Enthalpies of Solution For Methane From the Literature

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_{\text{solv.}}, \text{ Kcal/mol of gas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frank and Evans (1945)</td>
<td>-3.18</td>
</tr>
<tr>
<td>Morrison and Johnstone (1954)</td>
<td>-3.21</td>
</tr>
<tr>
<td>Himmelbau (1959)</td>
<td>-3.17</td>
</tr>
<tr>
<td>Battino (1986)</td>
<td>-3.19</td>
</tr>
</tbody>
</table>

The enthalpies of solution are negative, which is in agreement with the literature. Please refer to table D.6. Previous reports gave the standard molar enthalpy of solution for pure methane, but they were at an atmospheric pressure. At lower temperature, the enthalpy of solution increases as the temperature approaches the catastrophic temperature $T_c$. Even before hydrate formation, the value found are much bigger than that at $P=1\ \text{Atm}$. This might be explained by the fact that, as the temperature gets closer to $T_c$, the change of enthalpy is compared to ice formation on one hand and to experimental heats of dissociation on the
other hand. In 1996, Feneyrou explained that the heat associated with the formation of one mole of liquid water from ice is at least 8 Kcal/mole of methane gas, present in the liquid water. Therefore, this heat might be compared to the change of enthalpy of solution as $T_c$ is approached. Moreover, the enthalpy of dissociation for methane gas hydrate at 2020 Psia is very close to the enthalpy of dissolution of the same gas when $T_c$ is approached. For a pressure of 560 Psia, the value obtained for pure methane, just before $T_c$, corresponds to the literature values found for the enthalpy of dissociation at the same conditions.

D.2.2 Entropy Change

Figures D.7 and D.8 give the entropies change for pure methane gas and pure carbon dioxide in pure water. The results obtained for pure methane gas seems to be consistent with the literature values since the entropy change increases with increasing pressure. However, the value found by Feneyrou does not really follow this rule. Concerning pure carbon dioxide, the literature values are also very scarce but a comparison with the value, found by Feneyrou, shows an agreement with these results.

Moreover, the entropies of solution in water for both components are negative by a large amount, as shown in the literature (Himmelblau, 1959; Wilhelm and Battino, 1977; Sloan, 1994).
Figure D.7. Entropies Change for Pure Methane
The partial molar entropy of solution is influenced by the size of the cavity, which is created by the gas molecules when an estimate of the cavity size is made by bond distances, (Himmelblau, 1959). Frank and Evans, (1945), and later, Song et al. (1996), have demonstrated that the large negative values for partial molar entropies of solution of non-polar gases in water can be understood as the creation of a more highly ordered state in water or “icebergs”. The larger molecule give the larger negative values with decreasing temperature. This effect is reversed with increasing temperature. As the temperature is increased, these quasi ice-like structures break up and the entropy becomes positive.

D.2.3 Enthalpy of dissociation

Sloan described the enthalpy of dissociation as “one of the most important physical properties of hydrates”. The heat of dissociation is defined as the heat required to convert crystalline structure hydrates into fluid phases of gas and liquid water. The most accurate way to measure this heat is via calorimetric measurements. Three authors actually measured these enthalpies: Rueff in 1985, Handa in 1985, and Lievois in 1987.

Table D.7 gives the standard molar enthalpies of dissociation for pure methane gas while Table D.8 gives the values obtained with the differential calorimeter. The pressure used in this work are much higher than the atmospheric pressure since the range is from 38 Atm to 137 Atm.
Table D.7. Standard Molar Enthalpies of Dissociation For Methane From the Literature

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta H_{\text{disso.}, \text{Kcal/mol of gas}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roberts et al. (1941)</td>
<td>12.99</td>
</tr>
<tr>
<td>Deaton and Frost (1946)</td>
<td>13.17</td>
</tr>
<tr>
<td>McLeod and Campbell (1961)</td>
<td>13.16</td>
</tr>
<tr>
<td>Davidson (1973)</td>
<td>12.83</td>
</tr>
<tr>
<td>De Roo et al. (1983)</td>
<td>16.22</td>
</tr>
<tr>
<td>Kuuutra and Hammerschaib (1983)</td>
<td>12.43</td>
</tr>
<tr>
<td>Rueff (1985) *</td>
<td>12.86</td>
</tr>
<tr>
<td>Handa (1985) *</td>
<td>12.95</td>
</tr>
<tr>
<td>Lievois (1987) *</td>
<td>13.09</td>
</tr>
<tr>
<td>Holder (1988)</td>
<td>13.49</td>
</tr>
</tbody>
</table>

Therefore, the values obtained for the enthalpies of dissociation at these pressures are higher than at a pressure of 1 Atm. For $P=560$ Psia, (38 Atm), the value, which is in Table D.8, is the enthalpy of solution just before $T_c$, since the values found after $T_c$ are far from the literature values. From this table, the enthalpy of dissociation increases with increasing pressure, hence are consistent with the standard values obtained in the literature (Table D.7).
Table D.8. Molar Enthalpies of Dissociation For Methane at Different Pressures

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>Ramping Rate(°C/hr)</th>
<th>$\Delta H_{disso}$, Kcal/mole of gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>0.6</td>
<td>-16.74</td>
</tr>
<tr>
<td>1520</td>
<td>1.2</td>
<td>-20.68</td>
</tr>
<tr>
<td>1520</td>
<td>2.4</td>
<td>-21.47</td>
</tr>
<tr>
<td>2020</td>
<td>1.2</td>
<td>-26.02</td>
</tr>
</tbody>
</table>

For pure carbon dioxide, the value found for $\Delta H_{disso}$ is:

$$\Delta H_{disso} = -22.10 \text{ KCal/mole of gas at } P=560 \text{ Psia.}$$

This value is consistent with the study made by Sloan. He proved that the heat of dissociation, above 273.15 K, depends on the type of cavity occupied.

In fact, it seems to be that $\Delta H_{disso}$ may be approximated by the knowledge of the size of the hydrate guest molecule, since the heat of dissociation is assumed to be independent of the type and concentration of the guest gas. Methane forms hydrates in both cavities of structure I while carbon dioxide forms almost exclusively in the large cavities of structure I. Therefore, the enthalpy of dissociation for carbon dioxide may be larger than the enthalpy of dissociation for methane. This is observed in our results since $\Delta H_{disso} = -16.74 \text{ Kcal/mole of gas}$ for methane gas. However, in 1991, Fleyfel and Devlin suggested that carbon dioxide forms almost exclusively in the smaller cavities of structure I.
From this study, it appears that, since the heat of dissociation depends largely on the type of cavity occupied, a dominant role is played by the water hydrogen bonds in the host cages. Moreover, since the enthalpy also depends on the variables affecting adsorption, it is also a function of the pressure and temperature as well as the sight (cage size). In the following part, a study of the hydration number gives some new informations on the stability of the cages and the hydrate structures.
E. INFLUENCE OF HYDRATION NUMBER ON THE STABILITY OF HYDRATES

E.1 HYDRATION NUMBER

The general formula for hydrates is written as $M \cdot nH_2O$, where $nH_2O$ enclathrates a hydrate former $M$ and $n$ is the hydrate number, which depends on the pressure and temperature. Historically, the determination of the number of hydrate water molecules per guest molecule is divided into two periods. From 1810 to 1900, the hydration number was determined directly by using an experimental measurement of each amount of hydrated water and guest molecules. However, two experimental difficulties occurred. The water phase could not be completely converted into the hydrate without some occlusion, and the reproducible measurements of the inclusion of the guest molecule was hindered by metastability. Therefore, the hydration numbers differed widely for each substance. Following this period, the direct determination was abandoned in favor of the indirect method, which was originally proposed by de Forcrand in 1902. This method is still used today and is based on the calculation of the enthalpies of formation of hydrate from gas and water and from gas and ice. This method has been found to be much more accurate than the direct method. This is due to the determination of the heats of formation from the three-phase ($L_w-H-V$ or $I-H-V$) equilibrium measurements of pressure and temperature via the Clapeyron equation.
The Clapeyron Equation is: \[ \frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \]

where \( \Delta H \) is taken as the enthalpy change, \( \Delta V \) is the corresponding volume change.

This method was employed in 1946 by Deaton and Frost who used the heats of formation per mole of combined gas of the hydrate from two initial states: liquid water plus gas and ice plus gas. The difference between these two heats represented the heat of fusion of water present in the hydrate with 1 mole of gas. Dividing by the heat of fusion of 1 mole of water, they obtained the number of moles of water per mole of gas in the hydrate, thus the hydrate number.

In 1964, Saito, Marshall and Kobayashi measured the hydrate number of methane gas by observing the pressure drop in a closed system during hydrate formation. Their equations are based on the classical statistical thermodynamics theory of van der Waals and Platteeuw. In 1968, Galloway and Kobayashi used two different methods to determine the hydrate number. One is based on the calculation of the difference in number of moles of free gas in a closed system (as determined by P-V-T changes) before and just after the complete conversion of gas and liquid water phases to gas hydrate. The other one is based on the direct measurement of the volume of gas evolved during hydrate decomposition at constant pressure to get the number of moles of gas in the hydrate.
In this work, the method used was to measure the volume of gas evolved during a complete temperature-ramping cycle, at constant pressure. Therefore, the hydrate number was determined by using the solubility of the gas in the liquid phase. The following procedure was followed to get $N_{\text{cal}}$.

Let's consider $n_{j}^{I}$ the number of moles of J (Gas or Water) in phase I, and the following parameters:

$$S = \text{Solubility in the liquid phase} = \frac{n_{G}^{L}}{n_{W}^{L}}$$

$$W = \text{Total moles of water in the system} = n_{W}^{L} + n_{W}^{H}$$

$$G = \text{Total moles of gas in the condensed phase after hydrate formation} = n_{G}^{L} + n_{G}^{H}$$

$N_{\text{th}} = \text{Theoretical Hydration Number}$

$$N_{\text{th}} = \frac{[\text{Number of water molecules}]}{[(6 \times \text{large cavities occup}) + (2 \times \text{small cavities occup})]}$$

$N_{\text{cal}} = \text{Calculated Hydration Number} = \frac{n_{W}^{H}}{n_{G}^{H}}$
This method implies an uniform filling throughout the hydrate sample. A complete occupancy of the geometrically available cavities implies \( N_{th} = 5 \frac{3}{4} \).

By simplifications, the number of moles of free water in the liquid phase after hydrate formation is equal to:

\[
n_W^L = \frac{(N_{th} \cdot G - W)}{(N_{th} \cdot S - 1)}
\]

Knowing this amount, the number of moles of water in the hydrate phase is equal to:

\[
n_W^H = W - n_W^L
\]

and the amount of hydrates formed:

\[
\%H = \frac{n_W^H}{W}
\]

Therefore, the hydration number is equal to:

\[
N_{cal} = \frac{n_W^H}{G - n_G^L}
\]

The values of \( S, G \) and \( W \) are read on the spreadsheet. See appendix B for an example of calculation with pure methane.

**E.1.1 METHANE HYDRATE**

Tables E.1 through E.3 give the hydration numbers found for methane hydrates at different pressures and ramping rates. The results of \( N_{cal} \sim 6.00 \) are in general agreement with the consistent values reported in the literature. Please refer to Table E.4 for comparison with the literature. The values obtained suggest an incomplete occupancy of the 12-hedral and 14-hedral cages of structures I since it is far from the asymptotic value of \( 5 \frac{3}{4} \).
Table E.1. Hydration Number for Methane-Water System with $P=3.86$ MPa (560 Psia)

<table>
<thead>
<tr>
<th></th>
<th>Ramping rate=0.6 °C/hr</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run#1</td>
<td>Run#2</td>
<td></td>
</tr>
<tr>
<td>Moles of water in Hydrate</td>
<td>2.15</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>Moles of Methane in Hydrate</td>
<td>0.35</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Hydrate formed (%)</td>
<td>7.80</td>
<td>8.06</td>
<td></td>
</tr>
<tr>
<td>Hydration Number</td>
<td>6.15</td>
<td>6.16</td>
<td></td>
</tr>
</tbody>
</table>

Table E.2. Hydration Number for Methane-Water System with $P=10.48$ MPa (1520 Psia)

<table>
<thead>
<tr>
<th></th>
<th>Ramping rate=1.2 °C/hr</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run#1</td>
<td>Run#2</td>
<td></td>
</tr>
<tr>
<td>Moles of water in Hydrate</td>
<td>1.62</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>Moles of Methane in Hydrate</td>
<td>0.27</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Hydrate formed (%)</td>
<td>4.50</td>
<td>5.06</td>
<td></td>
</tr>
<tr>
<td>Hydration Number</td>
<td>6.04</td>
<td>6.01</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ramping rate=2.4 °C/hr</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run#1</td>
<td>Run#2</td>
<td></td>
</tr>
<tr>
<td>Moles of water in Hydrate</td>
<td>3.14</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>Moles of Methane in Hydrate</td>
<td>0.53</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Hydrate formed (%)</td>
<td>8.72</td>
<td>6.03</td>
<td></td>
</tr>
<tr>
<td>Hydration Number</td>
<td>5.96</td>
<td>5.98</td>
<td></td>
</tr>
</tbody>
</table>
### Table E.3. Hydration Number for Methane-Water System with \( P = 13.931 \) MPa (2020 Psia)

<table>
<thead>
<tr>
<th></th>
<th>Run#1</th>
<th>Run#2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of water in Hydrate</td>
<td>10.98</td>
<td>8.77</td>
</tr>
<tr>
<td>Moles of Methane in Hydrate</td>
<td>1.81</td>
<td>1.45</td>
</tr>
<tr>
<td>Hydrate formed (%)</td>
<td>30.50</td>
<td>24.36</td>
</tr>
<tr>
<td>Hydration Number</td>
<td>6.07</td>
<td>6.03</td>
</tr>
</tbody>
</table>

### Table E.4. Hydration Number for Methane-Water System from the Literature

<table>
<thead>
<tr>
<th></th>
<th>Methane: CH4-nH2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>De Forcrand</td>
<td>6.00</td>
</tr>
<tr>
<td>Villard</td>
<td>/</td>
</tr>
<tr>
<td>Hammerschmidt</td>
<td>6.00</td>
</tr>
<tr>
<td>Roberts et al.</td>
<td>7.00</td>
</tr>
<tr>
<td>Deaton and Frost</td>
<td>7.18</td>
</tr>
<tr>
<td>Glew</td>
<td>5.77</td>
</tr>
<tr>
<td>Galloway et al.</td>
<td>6.00</td>
</tr>
<tr>
<td>Lievois</td>
<td>6.04</td>
</tr>
<tr>
<td>De Roo</td>
<td>6.30</td>
</tr>
<tr>
<td>Handa</td>
<td>6.00</td>
</tr>
</tbody>
</table>
However, it has to be opposed to the value found by Glew in 1962, $N_{\text{cal}} = 5.77$, which suggest a nearly complete occupancy under equilibrium conditions at 273 K. Only Lievois and Handa used a differential calorimeter and actually directly measured the pure methane hydrate dissociation enthalpy in order to get the occupation number.

Moreover, the reproducibility of the hydrate number for each run at different pressures is well verified. The hydrate number increases slightly with increasing pressure, which was also verified by Galloway. Please refer to table E.5. Qualitatively, these results conflict with the theoretical prediction that the hydrate numbers should decrease with increasing pressure. The theoretical prediction is based on the solid solution theory of van der Waals and Platteeuw, who assumed the Lennard-Jones and Devonshire potential to evaluate the cell partition function $h_{K\text{~}i}$. It determines the Langmuir constants $C_{K\text{~}i}$, hence the hydrate number. This method has been used by Saito, Marshall and Kobayashi in 1964 for methane hydrate for a pressure range of 382 to 15,000 Psia.

Table E.5. Experimental hydrate numbers for methane hydrates obtained by Galloway (1968)

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>1030</th>
<th>1902</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ($^\circ C$)</td>
<td>10.0</td>
<td>15.6</td>
</tr>
<tr>
<td>Method I</td>
<td>5.84</td>
<td>6.19</td>
</tr>
<tr>
<td>Method II</td>
<td>6.16</td>
<td>6.34</td>
</tr>
<tr>
<td>Solid solution Theory</td>
<td>6.30</td>
<td>6.14</td>
</tr>
</tbody>
</table>
However, the error analysis of the calorimeter shows that a high precision is needed for all of the measurements. Therefore, it will be necessary to determine the hydrate numbers over a much larger range of pressure in order to verify or refute the solid solution theory for pure component hydrates. This work must be expanded to larger pressures in order to get a better understanding of the influence of the pressure on the hydration numbers for different gases.

**E.1.2 CARBON DIOXIDE HYDRATE**

Table E.6 gives the hydration number obtained for pure carbon dioxide at 560 Psia with a ramping rate of 0.6° C/hr. After many attempts, 0.6° C/hr appeared to be the only ramping rate which allowed a complete cooling/heating cycle. In this experiment, the value found, 7.8, is in general agreement with the literature value.

<table>
<thead>
<tr>
<th>Table E.6. Hydration Numbers for Carbon Dioxide-Water System with P=3.86 MPa (560 Psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ramping rate=0.6 C/hr</strong></td>
</tr>
<tr>
<td>Run #1</td>
</tr>
<tr>
<td>Moles of water in Hydrate</td>
</tr>
<tr>
<td>Moles of Carbon Dioxide in Hydrate</td>
</tr>
<tr>
<td>Hydrate formed (%)</td>
</tr>
<tr>
<td>Hydration Number</td>
</tr>
</tbody>
</table>
The scarce literature values are given in the table E.7. The values are between 6 and 7. However, Yamamuro and Suga, in 1989, measured or estimated the hydration number between 6 and 9. Therefore, the tolerance for hydration numbers for pure carbon dioxide appears to be larger than for pure methane, which was around 6 for most of the experiments.

Table E.7 Hydration Numbers for Carbon Dioxide-Water System from the Literature

<table>
<thead>
<tr>
<th>De Forcrand</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villard</td>
<td>6.0</td>
</tr>
<tr>
<td>Deaton and Frost</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The value found is very interesting since global warming could be limited by transforming carbon dioxide gas on earth, in gas hydrates, and depositing these hydrates in the deep ocean. For required conditions of temperature and pressure, the carbon dioxide hydrates will not decompose, hence limiting a substantial warming of the earth.

Moreover, the carbon dioxide hydrate number, obtained in this experiment, shows an incomplete occupancy of the 12-hedral and 14-hedral cages of structure I since the value is far from the ideal value 5 3/4. Moreover, this incomplete occupancy is larger than for the pure methane. This could be explained by the fact that carbon dioxide hydrates were more difficult to form than
methane hydrates. The limited literature data for carbon dioxide hydrates are not sufficient to explain a dependence of the hydrate number on the pressure, as is the case with pure methane. Therefore, it was not possible to compare with the solid solution theory. Higher pressures should be used for carbon dioxide in order to verify this theory. However, as mentioned earlier, we refer to the value $n$ as an asymptotic value, which is not definable precisely so long as it follows an adsorption type relationship.

E.2 MECHANISM OF CAVITY FORMATION

The water molecules has four charges. Two positive charges are given by the shared electrons with the protons and two negative charges are formed by the lone pairs of electrons. Therefore, each water molecule can be attached to four other water molecules through four hydrogen bonds by donating two and receiving two. According to Pauling and Kanavau, in high-pressure and low-temperature, a large amount of water molecules exists in a form of hydrogen-bonded, multimembered clusters due to molecular interactions and hydrogen bonding. In most of these clusters, water molecules are bonded weakly and such clusters are unstable under their own attractive forces. The clusters, which are relatively stable, are those with ring structures, pentagonal or hexagonal. In this case, hydrogen bonds tend to share edges in order to form polyhedral cavities.
The cavities related to methane or carbon dioxide are pentagonal dodecahedra ($5^{12}$), tetrakaidecahedra ($5^{12} 6^{2}$) or hexakaidecahedra ($5^{12} 6^{4}$).

In these cavities, the water molecules have their hydrophobic sides to the inside (i.e. no proton or lone electron pair is arranged to the inside) and hydrophilic sides to the outside. This arrangement is thermodynamically favorable for one cavity to share edges and faces with other cavities. Therefore, the stability of the cavities in structures I and II depends on the hydrogen-bond energy and on the geometric distortions.

Moreover, the tetrahedral structure of ice is known to have the highest stability among the crystalline structures formed by water molecules. However, structures I and II, which also have tetrahedral frameworks, are not as stable as ice. This is due to two factors. First of all, structures I and II have planar pentagonal rings, which have an unfavorable angle for hydrogen bonding and less degree of freedom [Luck, 1976], whereas the ice is formed by non-planar hexagonal rings having the maximum hydrogen-bond energy. Secondly, the tetrahedral angles of ice are arranged in an optimum way that there is almost no geometric distortion, whereas the angles of structure I or II have a departure of a few degrees (around $3.0^\circ$) from those of ice, hence resulting in geometric distortions that destabilizes the cavities.

Therefore, the three types of cavities are unstable in nature, due to the weak hydrogen bonding and to the geometric distortions.
E.3 STABILITY OF METHANE AND CARBON DIOXIDE HYDRATE

In CH$_4$/CO$_2$-water systems, the unstable cavities can be stabilized by the filling of CH$_4$/CO$_2$ molecules (as guests) in these cavities (as hosts). The free diameters for the $5^{12}$, $5^{12}6^2$, and $5^{12}6^4$ cavities are, respectively, 4.92 Å, 5.76 Å and 6.46 Å [Sloan, 1990]. Since the van der Waals diameter for the CH$_4$ molecule is 4.36 Å, CH$_4$ molecules can easily occupy each of these cavities. However, CH$_4$ molecules more easily occupies the cavities of structure I. Moreover, the van der Waals diameter for the CO$_2$ molecule is 5.12 Å. Therefore, CO$_2$ molecule can easily occupy a $5^{12}6^2$ cavity or a $5^{12}6^4$ cavity but has some difficulties entering a $5^{12}$ cavity. During cavity formation, CO$_2$ molecules might be encaged in this type of cavity but will have to break it in order to get out. Since CO$_2$ can occupy 75% of the cavities of structure I and only 33% of the structure II [Teng, 1995], structure I will be the most common structure for CO$_2$ hydrate. CO$_2$ will occupy the largest cavities of structure I.

According to Sloan, the motion of the gas molecule in an occupied cavity is rotational. Since water molecules, which formed the cavity, have their protons and lone electrons pairs arranged to the outside, the dynamic interactions
due to the collisions and the interactions between permanent-dipole and induced-dipole are limited. Therefore, the interactions between the gas molecule and the cavities occupied are mainly due to van der Waals forces. To stabilize a hydrate structure, every cavity does not have to be occupied. A cavity can be stabilized by van der Waals forces, from a CH$_4$/CO$_2$ molecule in the cavity or from CH$_4$/CO$_2$ molecules in the neighboring cavities.

The mechanism of instability of CO$_2$ hydrate may be explained by the fact that the $5^{12}$ cavities are statistically empty, hence unstable, since the van der Waals diameter for CO$_2$ is too large to fit this cavity. Moreover, if the distorted tetrahedral angles are not modified at one of the vertices of a $5^{12}$ cavity, then this vertex is unstable and results in the instability of the entire cavity. Since the cavities are associated through face and edge sharing, the instability of an empty $5^{12}$ cavity leads to the instability of the entire hydrate structure. Therefore, CO$_2$ hydrates are only stable when all the distorted tetrahedral angles are modified [Sloan, 1990- Teng, 1995]. Teng proposed the following criteria for the stability of CO$_2$ hydrates in the cavities:

$$y \geq 5 \text{ or } \eta \geq 62.5\% \text{ where } \eta = \frac{(x + y)}{8} \text{ is the occupancy.}$$

For a complete occupancy, $(x+y)=8$, $\eta=100\%$ and the hydration number equals 5.75.
It has been shown that an occupancy larger than 62.5% is enough to insure the stability of the carbon dioxide hydrate. This implies that the hydration number is in the range: 5.75-9.2.

Concerning the stability of methane hydrate, a similar criteria might be applied. However, the literature shows a hydration number for methane gas between 6 and 7. Therefore, the criteria may be:

\[ \eta \geq 75\% \text{ where } \eta = \frac{x + y}{8} \text{ is the occupancy} \]

The best value of hydration number, obtained with the calorimeter for carbon dioxide, has been added to his table. Please refer to Table E.8. This value fits perfectly in this table, showing a consistent experimental result for carbon dioxide. The occupancy is 73.5%, showing a relative stability, according to this criteria. A guest/cavity size ratio of approximately 75% is necessary for the stability of gas hydrate.

**Table E.8. Hydration Numbers and Occupancy for Carbon Dioxide**

<table>
<thead>
<tr>
<th>N</th>
<th>5.75</th>
<th>6.57</th>
<th>7.67</th>
<th>7.80</th>
<th>9.2</th>
<th>11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta%$</td>
<td>100</td>
<td>83</td>
<td>75</td>
<td>73.5</td>
<td>62.5</td>
<td>50</td>
</tr>
<tr>
<td>$x_{CO_2}^H$</td>
<td>0.148</td>
<td>0.132</td>
<td>0.115</td>
<td><strong>0.113</strong></td>
<td>0.098</td>
<td>0.080</td>
</tr>
</tbody>
</table>
For pure methane, the guest/cavity size ratio, (or occupancy), is 95%. Therefore, methane hydrate is stable in the cavities of structure I.

Therefore, this study shows that both methane and carbon dioxide are non-stoichiometric compounds. Moreover, the three cavities, $5^{12}$, $5^{12} 6^2$, and $5^{12} 6^4$, appear to be unstable in nature, since the hydrogen bonding is weak and the geometric distortions does not fully stabilize them. A cavity can be stabilized by van der Waals forces, from a methane (or carbon dioxide) molecule in the cavity or from methane (or carbon dioxide) molecules in the neighboring cavities. A criteria of stability has been proposed by Teng, which show the reliability of the results obtained in this work. Both components appear to be stable.

Moreover, the limits of stability of the liquid solution of methane (or carbon dioxide) in water depends on the Gibbs free energy change of mixing in the gaseous and liquid phases. Gibbs free energy was studied, earlier, by Heidemann, in 1974, Baker et al., in 1982, and Myerson and Sencel, in 1984. The limits of stability are defined by the following relation:

$$\frac{\partial^2(\Delta G_{mix})}{\partial^2(x_1^2)} = \frac{\partial(\ln f_1)}{\partial x_1} = 0$$

where $f_1$ is the fugacity of pure methane in liquid or gaseous state. However, these limits do not give any information concerning the appearance of a solid phase from the liquid solution.
A study, made by Englezos in 1988, shows that the clustering process of water molecules, which enclose methane molecules, could deplete methane in the bulk liquid phase, hence more methane will dissolve. Once the clusters have reached a critical size, they become more stable and appear as nuclei. This is the end of the primary nucleation. For more details concerning the kinetic process of hydrate formation, please refer to section F.

Moreover, both components occupy the cavities of structure I, even if carbon dioxide may occupy the larger ones, since the van der Waals diameter of carbon dioxide is larger than of methane. A guest molecule must be big enough to provide stability for the cavity, but not so big that it cannot fit. When the ratio is less than 75% by a large amount, the molecule cannot offer enough stability to the cavity in order to insure the hydrate formation. Therefore, the fit of the molecules in the cavities is essential to the structure and to the equilibrium properties of hydrates.

The next section deals with the mechanisms and kinetics of the hydrate formation and decomposition.
F. MECHANISMS AND KINETICS OF HYDRATE FORMATION AND DECOMPOSITION

F.1 MECHANISMS AND KINETICS OF HYDRATE FORMATION

F.1.1 MECHANISM OF HYDRATE FORMATION

In 1994, Sloan postulated that the labile clusters played an essential role in the hydrate formation. A labile cluster is defined as the organization of the water molecules around the apolar molecule when an apolar gas dissolves into water. The number of molecules which participate in these clusters depends on the size of the gas molecule.

Figure F.1 gives a visual model of the hydrate formation. It shows the evolution of the gas molecules from the initial conditions (A), to the formation of labile clusters (B), to a metastable agglomeration (C), and to a stable nuclei (D) when the size of the clusters agglomerates has reached a critical value. Thus, D is the end of the primary nucleation and the beginning of the growth.

A more complete cycle is given in Figure F.2 with a pressure-temperature diagram at constant volume:

1. Formation starts. Gas molecules are dissolved into water and labile clusters start forming around the apolar guest molecules.
Figure F.1. Visual Model of the Hydrate Formation

A. Initial Condition
Pressure and temperature in hydrate forming region, but no gas molecules dissolved in water

B. Labile Clusters
Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration
Labile clusters agglomerate by sharing face, face increasing disorder.

D. Primary Nucleation and Growth
When the size of cluster agglomerates reaches a critical value, growth begins.

Figure F.2. Diagram of the Hydrate Formation on an Experimental Pressure-Temperature Trace

(Source: Christiansen and Sloan, 1994)
(1)-(2) Clusters link together in order to form aggregates in the metastable cooling region, by sharing faces.

(2) Clusters have reached the critical size needed for nucleation. The primary nucleation is terminated and a rapid hydrate growth follows. This is shown by a rapid drop in pressure on this diagram, due to the encapsulation of gas molecules in the hydrate.

(3) End of the growth period. The hydrate formation stops and the system is heated until the point A. During these two points, the hydrate agglomerates start decomposing into the liquid and vapor phases. However, the quasi-crystalline cluster structures are still in the liquid phase until a certain degree of superheating is administered.

In this work, the results, concerning the behavior of the solubility for the pure components with temperature, show the same steps of the process of hydrate formation. During the primary nucleation (1 to 2), the solubility increases slowly and the divergence with Henry's Law is more and more pronounced. At Tc, (2), the crystal growth starts and a sudden and fast increase of the solubility of methane, carbon dioxide, and methane (5%)-carbon dioxide in pure water is observed. Please refer to Figure C.21 to C.25.

Moreover, in the hydrate formation process, the coordination number of the labile clusters in the liquid phase determines the composition of the dissolved gas molecules.
For the case of methane, the labile clusters will have a coordination number of 20. In order to obtain the needed set of coordination numbers for the labile clusters, some clusters will be transformed, following a process, which requires the forming and breaking of hydrogen bonds via an activation energy. The height of the activation energy barrier will affect the rate of transformation, hence the rate of hydrate formation. This height of activation will depend on the composition of the dissolved gas and on the coordination number, which has to be obtained.

**F.1.2 KINETICS OF HYDRATE FORMATION**

An understanding of the kinetics of hydrate formation is an important factor in explaining the hydrate structures. Due to the high degree of metastability, which occurs during the nucleation of the crystal, experimental kinetic studies are quite difficult. On the contrary, kinetic studies of hydrate dissociation are easier since the dissociation process does not exhibit high levels of metastability.

Concerning the study of crystal growth, several authors had worked on this step of the hydrate formation process: Miller and Smythe, in 1970, followed by Falabella in 1975, Bishnoi and co-workers in 1980, and Englezos et al. in 1988. In 1982, Vysniauskas and Bishnoi studied the kinetic of methane hydrate formation, using a semi-batch stirred tank reactor, operated in isothermal and isobaric modes. The experiment was designed to measure the volumetric consumption rate of methane gas during hydrate formation, after primary nucleation.
The experiments were run for 15 min. or until 5% of water was transformed into gas hydrates. His experiments shows that the volume of gas consumed in the standard conditions of pressure and temperature increases drastically with the increasing stirring rate, for a range of 300 rpm to 600 rpm. This may be due to the fact that the surface area of contact between the gas and the water increases with an increasing stirring rate. Moreover, he visually observed that, at 300 rpm, the hydrate crystals have a tendency to stay on the surface area between the gas and water. However, for a larger stirring rate, i.e. 400 rpm, the agitation is sufficient to remove these crystals from the surface area. Therefore, the kinetic process of gas hydrate formation is function of the stirring rate, which increases or decreases the consumption rate of gas, for a larger or smaller stirring rate.

The results, obtained with the calorimeter, are based on a stirring rate of 300 rpm, which is the maximum rate for the calorimeter. After 15 min., just after Tc, the following increase of solubility of pure methane gas in liquid phase have been calculated.

Table F.1. Increase of Methane Gas Consumption After 15 Minutes with a Stirring Rate of 300 RPM

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>Ramping Rate (°C/hr)</th>
<th>$\Delta X_{CH_4} \times 1000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>0.6</td>
<td>0.26</td>
</tr>
<tr>
<td>1520</td>
<td>1.2</td>
<td>0.23</td>
</tr>
<tr>
<td>2020</td>
<td>1.2</td>
<td>0.22</td>
</tr>
</tbody>
</table>
For the same stirring rate and a pressure of 798 Psia, Vysniaukas found a methane gas consumption of $\Delta X_{CH_4} \times 1000 = 1.85$. Therefore, the rate of formation in the cell of the calorimeter is much slower than in the tank reactor, used by Vysniauskas. However, he worked at very low temperature, 1.15°C, much lower than the temperatures reached with the calorimeter, around 4.5°C for 1520 Psia and 5.0°C for 2020 Psia. The displacement range of the plungers would not allow such low temperatures.

Moreover, this table shows that the consumption rate of methane gas at 560 Psia is more important than the one at 1520 Psia or 2020 Psia. This could be explained by the fact that the ramping rate is the main effect of this tendency. As seen previously, a slower ramping rate insures hydrate formation, hence increasing gas consumption just after $T_c$. However, even if a slow ramping rate facilitates the hydrate formation, the overall rate of hydrate formation depends mainly on the pressure, hence the rate increases with increasing pressure. This is proved in Table F.2.

The rate of hydrate formation for pure methane is in agreement with the value found by Feneyrou. As is shown in the table, a pressure of 2020 Psia allows a formation of 30.5%, which is much larger than 8.1% obtained at 560 Psia, even if the ramping rate was slower for 560 Psia.
Table F.2. Percentage of Hydrate Formation

<table>
<thead>
<tr>
<th>Pressure (Psia)</th>
<th>Ramping Rate (°C/hr)</th>
<th>%H Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feneyrou</td>
<td>500</td>
<td>1.0</td>
</tr>
<tr>
<td>This Work</td>
<td>560</td>
<td>0.6</td>
</tr>
<tr>
<td>This Work</td>
<td>1520</td>
<td>1.2</td>
</tr>
<tr>
<td>This Work</td>
<td>1520</td>
<td>2.4</td>
</tr>
<tr>
<td>This Work</td>
<td>2020</td>
<td>1.2</td>
</tr>
</tbody>
</table>

In 1988, Englezos et al. measured the consumption of methane as a function of time prior to the secondary nucleation, which was called the hydrate nucleation or "turbidity point". They found that methane was supersaturated in the solution as a function of time. This supersaturation is required for the formation of gas hydrates to occur. Therefore, the time, which is required for increasing the solubility and for reaching the critical nucleus size, is comparable to the time required during hydrate metastability. Their model is based on the kinetics of crystallization, which means two distinct processes: nucleation and growth. Nucleation and growth are going to occur at the gas-water interface, where the supersaturation is the greatest in the liquid water phase. Their study reveals that the rate of formation is proportional to the difference in fugacity of the dissolved gas and of the three-phase equilibrium fugacity at the experimental temperature.

In 1989, Lingelem and Majeed tried to quantify the time required for the crystals to appear in a sapphire cell at high pressure.
It appears that the most likely place for the hydrate crystals to grow was located at the gas-water interface, at the boundary of the macroscopic aqueous liquid phase.

The results, obtained from this study with the calorimeter, are in general agreement with the literature even if it was not possible to reach the low temperatures used. The experiments should have been tried at much higher pressure in order to insure higher gas consumption rates. However, the scope of this thesis was not to cover a so large range of pressure, hence further work still has to be done in this area.

Moreover, the kinetic process, in two phases: nucleation and growth, has been studied by several authors but its understanding is still incomplete. For instance, very few kinetics data have been obtained with high amounts of inhibitors. Therefore, since the determination of the rate of hydrate formation is somewhat inaccurate, further studies should complete what has been done, concerning the kinetics data.

F.1.3 STUDY TO FOLLOW ACTUAL CRYSTALLIZATION PROCESS

The crystallization of a solute from a liquid phase is a well-known process, which requires the presence of sufficient supersaturation. Englezos et al., in 1987, observed that the liquid water was supersaturated before the appea-
rancce of the hydrate nuclei. At the nucleation point, the solubility of methane gas in liquid water exceeded by far the solubility corresponding to the three-phase equilibrium pressure and the one to the gas-liquid equilibrium, as determined by Henry's Law. He used the Gibbs free energy (Treble-Bishnoi equation of state) to determine the limits of stability of methane. The experimental points define the spinodal curve, which is the curve between metastability and instability region. At isobaric conditions, these limits increase with temperature. The increase of solubility at the nucleation point may be explained by the clustering process which leads to the nucleation.

The first step of this crystallization process involves the primary nucleation process. This is a microscopic phenomenon, which involves a multitude of molecules, hence difficult to observe experimentally. This phenomena may be explained by the phenomenon of freezing water, the dissolution of hydrocarbons in water and the computer simulation of these liquid phenomena. In 1876, nucleation thermodynamics was initiated by Gibbs. Later, Volmer and Weber, in 1926, explained that kinetics played a major role in nucleation process, by the growth and decay of clusters of molecules. However, the nucleation phenomena are more difficult to observe than the macroscopic thermodynamics properties, since it includes metastability, microscopic scales and time-dependence of kinetics. Therefore, most of the knowledge is conceptual.

In order to get a better understanding, the mechanism of water supercooling and freezing must be studied.
Two mechanisms exist: the first one is based on the liquid water flickering cluster mechanism or "iceberg" theory from Frank and co-workers. The most recent one is based on the liquid water "hydrogen-bonded network-cluster" mechanism, model proposed by Stillinger and Rahman, in 1973.

Frank described the water as an equilibrium mixture of short-lived ($\sim 10^{-10}$ s.) hydrogen-bonded clusters, with a non-hydrogen-bonded dense phase. In 1974, Makogon explained that the clustering of water molecules constitutes the beginning of hydrate nucleation. He used X-Ray diffraction to show the short-term clustering of water with decreasing temperature. The water clusters and guest molecules grow until a critical nucleus size is reached to enable the next step, which is the hydrate crystallization. The radius of this critical nucleus size is defined by Makogon as:

$$r_c = \frac{2\sigma T_c}{(\Delta H)(\Delta T)}$$

where $\Delta H$ is the latent heat of crystallization.

$\sigma$ is the "nuclei's specific surface energy".

$\Delta T$ is the degree of supercooling at a given three-phase equilibrium pressure.

Further studies, including those from Wall and Hornig, in 1965, suggest, by using Raman scattering, that water cannot be a mixture of large clusters and non-bonded molecules. Therefore, the hypothesis of "network-cluster" model
"appeared", mainly with Stillinger. Using molecular dynamics studies, he described water as a "macroscopically connected random network of hydrogen bonds, with frequent strained and broken bonds, that is continually undergoing topological reformation". Molecular dynamics is a statistical and mechanical technique to simulate water structures. The total energy, (kinetic and potential), and the velocity average, (temperature), of the system are determined, hence all of the others thermodynamics properties can be calculated for an isochoric system. This technique enables the study of time-dependent properties, such as nucleation. This technique has been validated through the comparison of calculated thermodynamics properties, such as the heat capacity or the maximum of the density. It appears that the sharing of polyhedra faces and edges in supercooled water suggests a pre-nucleation phenomenon for gas hydrates.

Therefore, different techniques have been tried in order to explain the crystallization process, but it appears that the molecular dynamics technique is the most accurate in showing the properties of supercooled water and the existence of a pre-nucleation phenomenon, prior to gas hydrate formation.
F.2 MECHANISM AND KINETICS OF HYDRATE DISSOCIATION

The dissociation follows the same scheme as described in Figure F.2, except in the opposite direction. Makogon presented data showing that during the dissociation process, hydrates do not totally decompose and leave a partial structure which will form more easily for a next cooling/heating cycle. In 1983, Vysniauskas and Bishnoi related the induction time for hydrate formation to the properties of water, (supercooling, etc.). The induction time is defined as the time elapsed between the start of the experiment and the appearance of the first hydrate crystal. Therefore, the hysteresis of the successive runs decrease, hence the metastability since residual hydrate structures are still present in the water.

This has been observed during the experiments conducted with the differential calorimeter, since the volume of gas added for a complete cycle was always smaller than for a previous run, where hydrate formation had occurred. Therefore, the hydrate formed more easily, since it did not totally decompose.

In 1987, Kim and co-workers studied the kinetic of hydrate decomposition by using a semi-batch stirred tank reactor. The decomposition was done by reducing the system pressure to a value below the three-phase equilibrium pressure at constant temperature. They found that the stirring time, required to obtain hydrate decomposition, is independent of the stirring rate. Moreover, the stirring speed appears to be function of the temperature and of the pressure of
decomposition. Therefore, higher temperatures and lower pressures require higher stirring speeds. Since the stirring rate was limited to 300 rpm for the calorimeter, the starting pressure should be as high as possible. The stirring rates were high enough to eliminate any mass-transfer effects. The decomposition rate appears to be proportional to the surface particle area and to the difference between the fugacity of the gas, (methane or carbon dioxide), at equilibrium, and the fugacity at the decomposition pressure.

The decomposition of solid hydrates is an endothermic process, which produces gaseous methane and liquid water. The overall process involves:

-- Destruction of the clathrate host lattice at the surface of a particle.
-- Desorption of the guest molecule (Methane or Carbon dioxide) from the surface.

Therefore, the kinetic process of formation and decomposition of gas hydrates is composed of four steps:

*** Nucleation

*** Crystal Growth

*** Destruction of the host lattice

*** Desorption of the guest molecule
Even after several authors worked on these different studies, much more work still has to be done. The thermodynamic determinations of pressure and temperature for formation/decomposition of gas hydrates appear to be more reliable than any kinetic studies. However, kinetic phenomena is a very important aspect to understand hydrate structure and rate of formation.
CONCLUSIONS

The heat flux calorimeter, designed and built by Lievois in 1987, has been modified somewhat. The computer/data acquisition network has been completely modified in order to allow isobaric, temperature-ramping experiments. The experimental procedure has enabled the elucidation of the discrete steps involved in the hydrate formation and decomposition of methane, carbon dioxide, and methane(5%)-carbon dioxide mixture at high pressure.

The measured volumes were utilized to determine directly the solubility of different gases in the water phase in a way that minimizes the uncertainties associated with the appearance of the solid hydrate phase. From this study, it has been confirmed that the solubility of gases in water, in the vicinity of the incipient hydrate formation temperature, is much greater than that would be predicted by Henry’s Law, the frequently used conventional calculation procedure. This divergence is explained by the high level of supersaturation that the system exhibits before the hydrate formation and by the high gas consumption rate when the crystal grows.

The measured electrical conductivity give very interesting and new results. The resistance values are function of the salt concentration but also of the temperature during the cooling/heating cycle.
Until the catastrophic temperature $T_c$, the resistance increases with decreasing temperature, showing a dependence on the various parameters $\Lambda_0$, S, E and J, rather than on the salt concentration. However, as soon as gas hydrates start forming, the resistance values are in agreement with the salt concentration, which follows the formation/dissociation steps of thehydrates by increasing when hydrates form and decreasing when hydrates decompose, since the amount of water increases in the liquid phase. In this work, the amount of water was determined via solubility measurements, since the salt concentration could not be measured directly while the temperature-ramping mode progresses.

The solubilities were also used to calculate some of the derived thermo-physical properties, such as changes of enthalpy of solution, entropy of solution, and mainly enthalpy of dissociation. These values provide a better understanding of the structure of the hydrates, an explanation of the mechanism of formation, primary nucleation, then growth of the crystals.

Moreover, the hydration numbers, for the different gases used, offer some criteria of stability of the cages in the host lattice for pure methane and pure carbon dioxide. The values found are in a very good agreement with the literature.

Finally, a kinetic study confirms the process of hydrate formation but is still incomplete for a thorough understanding of the hydrate formation/decomposition process.
More kinetics work should provide a complete understanding of hydrate formation, even if the high level of metastability makes this study difficult.

Future work on the calorimeter implies the use of inhibitors, such as methanol, for pure components and the study of more mixtures with methane and carbon dioxide. Moreover, an analysis of the structure of the hydrate via spectroscopy such as Raman spectroscopy may give some of real new informations on the process of hydrate formation/decomposition. Following the progress of the kinetics by spectrometric means would provide revealing understanding.
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APPENDIX A

Program for Control and Data Acquisition for the Calorimeter

Guillaume BESNARD
October 1996
Figure AX.1. Flowsheet of Temperature Measurement in the Cell and in the Block
Figure AX.2. Flowsheet of Pressure Control and Volume Measurement
Figure AX.3. Flowsheet of Electrical Conductivity Measurement
Figure AX.4. Flowsheet of Thermopile Measurement
VERSION 4.00

Attribute VB_Name = "CalorimeterForm"
Attribute VB_Creatable = False
Attribute VB_Exposed = False
Public HP%, keit%, stepper%, genrad%, b%, FileName$

Rem Used to count the time since start
Public minElapsed%, lastMinute%

Rem Declaration of the variables: Velocity, acceleration and volume
Public vel, accel, volume

Rem Set pressure and the last measured pressure
Public setPr, lastPressure

Rem Distinguish the first loop in the CalorITimer from the other runs
Public firstRun

Sub UpToRet(instrg$, result$)
  ' Return everything in instrg$ up to the first
  ' RETURN in result$. The first character in
  ' instrg is not considered.

  i% = 2
  c$ = Mid$(instrg$, 2, 1)
  While c$ <> Chr$(13)
    i% = i% + 1
    c$ = Mid$(instrg$, i%, 1)
  Wend
  result$ = Mid$(instrg$, 1, i% - 1)
End Sub
Sub UpToDot(instrg$, result$)

  ' Return everything in instrg$ up to the first
  ' "." in result$. The first character in
  ' instrg is not considered.

    i% = 2
    c$ = Mid$(instrg$, 2, 1)
    While c$ <> "."
        i% = i% + 1
        c$ = Mid$(instrg$, i%, 1)
    Wend
    result$ = Mid$(instrg$, 1, i% + 1)

End Sub

Static Sub ReportError(fd%, ErrMsg$)

  ' Stop the program when an error occurs and
  ' gives the type of error.

    Print "Error=", iberr%; ErrMsg$
    If (fd% <> 1) Then
        Print ("Cleanup: taking board offline")
        Call ibonli(fd%, 0)
    End If
    Stop

End Sub

Private Sub CaloriTimer_Timer()

    thisMinute% = Val(Mid$(Time, 4, 2))
    If (thisMinute% <> lastMinute%) Then
        minElapsed% = minElapsed% + 1
        lastMinute% = thisMinute%

        Minutes.Text = Str$(minElapsed%)

Print #1, Minutes.Text, ThermopileValue.Text, RTemperature.Text, LTemperature.Text, BTemp.Text, port2.Text, port1.Text, conductivity.Text,
Read the thermopile values from the HP multimeter

```
readinga$ = Space$(20)
Call ibclr(HP%)
Call ibwrt(HP%, "PRESET NORM")
Call ibwrt(HP%, "RES .00001")
Call ibwrt(HP%, "FUNC DCV")
Call ibrd(HP%, readinga$)
If (ibsta% And EERR) Then
    Call ReportError(HP%, "can't read from HP")
End If
RDAS$ = Left$(readinga$, ibcnt%)  
Call UpToRet(RDAS$, hresult$)
If Val(hresult$)<15 then
    ThermopileValue.Text = 100 * Left$(hresult$, 8)
else
    ThermopileValue.Text = 10 * Left$(hresult$, 8)
End If
```

Write to the Genrad
Get E.C. reading for frequency extrapolation
Read at F=1, 2, 4, 10 KHz

```
readinge$ = Space$(20)
readingf$ = Space$(20)
readingh$ = Space$(20)
readingi$ = Space$(20)
Call ibclr(genrad%)
```

Write to the genrad for F=1KHz

```
Call ibwrt(genrad%, "S2P0T1M3W1R5C0X6F1.0GO")
If (ibsta% And EERR) Then
    Call ReportError(genrad%, "can't write to Genrad for F=1")
End If
Call ibrd(genrad%, readinge$)
If (ibsta% And EERR) Then
```
Call ReportError(genrad%, "can't read from Genrad")
End If

RDES$ = Left$(readinge$, ibcnt$)
Call UpToRet(RDES$, Frequency1$)
conductivity1.Text = Right$(Frequency1$, 6)

Rem Write to the genrad for F=2KHz

Call ibwrt(genrad%, "S2P0T1M3W1R5C0X6F2.0GO")
If (ibsta% And EERR) Then
  Call ReportError(genrad%, "can't write to Genrad for F=2")
End If
Call ibrd(genrad%, readingf$)
If (ibsta% And EERR) Then
  Call ReportError(genrad%, "can't read from Genrad")
End If
RDFS$ = Left$(readingf$, ibcnt$)
Call UpToRet(RDFS$, Frequency2$)
conductivity2.Text = Right$(Frequency2$, 6)

Rem Write to the genrad for F=4KHz

Call ibwrt(genrad%, "S2P0T1M3W1R5C0X6F4.0GO")
If (ibsta% And EERR) Then
  Call ReportError(genrad%, "can't write to Genrad for F=4")
End If
Call ibrd(genrad%, readingh$)
If (ibsta% And EERR) Then
  Call ReportError(genrad%, "can't read from Genrad")
End If
RDHS$ = Left$(readingh$, ibcnt$)
Call UpToRet(RDHS$, Frequency4$)
conductivity4.Text = Right$(Frequency4$, 6)

Rem Write to the genrad for F=10KHz

Call ibwrt(genrad%, "S2P0T1M3W1R5C0X6F10.0GO")
If (ibsta% And EERR) Then
  Call ReportError(genrad%, "can't write to Genrad for F=10")
End If
Call ibrd(genrad%, readingi$)
If (ibsta% And EERR) Then
  Call ReportError(b%, "can't read from Genrad")
End If
RD1$ = Left$(readingi$, ibcnt%)
Call UpToRet(RD1$, Frequency10$)
conductivity10.Text = Right$(Frequency10$, 6)

Rem By least squares, we linearize SQR(1/F) and we extrapolate to 0
Rem i.e. we get infinite frequency

F1 = Right$(Frequency1$, 6)
F2 = Right$(Frequency2$, 6)
F4 = Right$(Frequency4$, 6)
F10 = Right$(Frequency10$, 6)

EC = (0.65107 * F1) + (0.06376 * F2) + (0.5694 * F4) + (1.0179 * F10)
EC = EC * 10
EC = (Int(EC)) / 10
conductivity.Text = Str$(EC)

Rem Read the PRT values in the left cell with the Keithley

ULStat% = cbDOut%(0, AUXPORT, 0)
If ULStat% <> 0 Then
  Stop
End If

readingb$ = Space$(20)
Call ibclr(keit%)
Call ibwrt(keit%, "F2R0Z0S7X")
Call ibrd(keit%, readingb$)
If (ibsta% And EERR) Then
  Call ReportError(b%, "can't read from Keithley")
End If
RDB$ = Left$(readingb$, ibcnt%)

Call UpToRet(RDB$, Lresult$)
Lresultval = Val(Mid$(Lresult$, 5, 16))

Rem Problem: Keithley sometimes gives a value
Rem which is by a factor of 1000 too large!

If (Lresultval > 900) Then Lresultval = Lresultval * 0.001
Ltemp = 3473.886 * (0.5 * (Sqr((48271510#) * (13996.6 * (Lresultval 499.641))))

temp = Ltemp
Ltemp = temp + 0.045 * (temp / 100) * ((temp / 100) 1) * ((temp / 419.58) 1) *
((temp / 630.74) 1)

LTemperature.Text = Left$(Str$(Ltemp), 6)

Rem Read the PRT values in the right cell with the Keithley

ULStat% = cbDOut%(0, AUXPORT, 1)
If ULStat% <> 0 Then
    Stop
End If
readingc$ = Space$(20)
Call ibclr(keit%)
Call ibwrt(keit%, "F2R0Z0S7X")
Call ibrd(keit%, readingc$)
If (ibsta% And EERR) Then
    Call ReportError(b%, "can't read from Keithley")
End If
RDC$ = Left$(readingc$, ibcnt%)

Call UpToRet(RDC$, Rresult$)
Rresultval = Val(Mid$(Rresult$, 5, 16))

Rem Problem: Keithley sometimes gives a value
Rem which is by a factor of 1000 too large!

If (Rresultval > 900) Then Rresultval = Rresultval * 0.001

Rtemp = 3421.99 * (0.5 * (Sqr((46840170#) * (13831.56 * (Rresultval 499.269)))))
temp = Rtemp
Rtemp = temp + 0.045 * (temp / 100) * (temp / 100 1) * (temp / 419.58 1) *
(temp / 630.74 1)

RTemperature.Text = Left$(Str$(Rtemp), 6)
Rem Equation not good for T<0 Deg.Celsius:

Rem A*T^2+B*T+C=0
Rem A=1
Rem B=(100+10000/DELTA)
Rem C=(10000/(RO*ALPHA*DELTA))*(KresultRO)
Rem
Rem LEFT CELL: ALPHA=3.9167795E3
Rem DELTA=1.4603279
Rem RO=499.641
Rem
Rem RIGHT CELL: ALPHA=3.9063495E3
Rem DELTA=1.4828021
Rem RO=499.269
Rem

Rem Read the values of the temperature in the surrounding block

If MSComm3.PortOpen <> True Then MSComm3.PortOpen = True

MSComm3.Output = Chr$(&H4) + "0000" + "PV" + Chr$(&H5)
Tdata$ = ""
Do
    Dummy = DoEvents()
    If MSComm3.InBufferCount > 0 Then Tdata$ = Tdata$ + MSComm3.Input
Loop Until (Right(Tdata$, 1) = Chr$(&H3)) Or (Right(Tdata$, 1) = Chr$(&H6))

BTemp.Text = Mid$(Tdata$, 4, 5)

MSComm3.InBufferCount = 0

Rem here ends the logging data per minute

End If

Rem Read the values of the pressure in the left cell

If MSComm1.PortOpen <> True Then MSComm1.PortOpen = True

'Sometimes the pressure transducers loose the Chr$(13)
'Let's catch this
pressureCount% = 0
MSComm1.Output = Chr$(13)
Pdata$ = ""
Do
    Dummy = DoEvents()
    If MSComm1.InBufferCount > 0 Then Pdata$ = Pdata$ + MSComm1.Input
    pressureCount% = pressureCount% + 1
    If pressureCount% = 1000 Then
        pressureCount% = 0
        MSComm1.Output = Chr$(13)
    End If
Loop Until Right$(Pdata$, 1) = Chr$(13)

Call UpToDot(Pdata$, result$)
port1.Text = result$

MSComm1.InBufferCount = 0

Rem Read the values of the pressure in the right cell

    If MSComm2.PortOpen <> True Then MSComm2.PortOpen = True

    'Sometimes the pressure transducers loose the Chr$(13)
    'Let's catch this

    pressureCount% = 0
    MSComm2.Output = Chr$(13)
    Pdata$ = ""
    Do
        Dummy = DoEvents()
        If MSComm2.InBufferCount > 0 Then Pdata$ = Pdata$ + MSComm2.Input
        pressureCount% = pressureCount% + 1
        If pressureCount% = 1000 Then
            pressureCount% = 0
            MSComm1.Output = Chr$(13)
        End If
    Loop Until Right(Pdata$, 1) = Chr$(13)

Call UpToDot(Pdata$, result$)
port2.Text = result$

P = Val(result$)
Po = setPr
If (P >= (0.9988 * Po) And P <= (1.0012 * Po)) Then
    P = Po
End If

If firstRun = 1 Then
    firstRun = 0
    lastPressure = P
Else
    If (1.2 * lastPressure < P Or 0.8 * lastPressure > P) Then
        Rem if the pressure changed by more than
        Rem 20% ignore this measurement
        P = lastPressure
    Else
        lastPressure = P
    End If
End If

If (P <> result$) Then
    P = lastPressure
End If

If (P < Po) Then
    diff% = Int(P / Po)
    distance = 2000.1 * diff%
    If (distance) < 10000 Then distance = 10000
    DSI$ = "D" + Str$(Int(distance))
    Rpump.Text = DSI$
    Q$ = "EMN A6.0 V6.0 L " + DSI$ + " ST1 G"
    Call ibwrt(stepper%, Q$)
    If (ibsta% And EERR) Then
        Call ReportError(stepper%, "can't write to stepper controller")
    End If
End If

If (P > Po) Then
    diff% = Int(P / Po)
    distance = 2000.1 * diff%
    If (distance > 10000) Then distance = 10000
    DSI$ = Str$(Int(distance))
    DSI$ = "D+" + Right$(DSI$, Len(DSI$) - 1)
Rpump.Text = DSI$

Q$ = "EMN A6.0 V6.0 L " + DSI$ + " ST1 G"
Call ibwrt(stepper%, Q$)
If (ibsta% And EERR) Then
   Call ReportError(stepper%, "can't write to stepper controller")
End If
End If

If (P = Po) Then
   Rpump.Text = 0
End If

End If

If (P < Po) Then
   diff% = Int(P Po)
distance = 2000.1 * diff%
If (distance) < 10000 Then distance = 10000
DSI$ = "D" + Str$(Int(distance))
Rpump.Text = DSI$

Q$ = "EMN A6.0 V6.0 L " + DSI$ + " ST1 G"
Call ibwrt(stepper%, Q$)
If (ibsta% And EERR) Then
   Call ReportError(stepper%, "can't write to stepper controller")
End If
End If

End If

If (P > Po) Then
   diff% = Int(P Po)
distance = 2000.1 * diff%
If (distance > 10000) Then distance = 10000
DSI$ = Str$(Int(distance))

DSI$ = "D+" + Right$(DSI$, Len(DSI$) - 1)
Rpump.Text = DSI$

Q$ = "EMN A6.0 V6.0 L " + DSI$ + " ST1 G"
Call ibwrt(stepper%, Q$)
If (ibsta% And EERR) Then
   Call ReportError(stepper%, "can't write to stepper controller")
End If

End If

If (P = Po) Then
    Rpump.Text = 0
End If

volume = volume  \(\frac{\text{distance}}{2500.5}\)
vol.Text = Left$(volume, 6)
MSComm2.InBufferCount = 0

End Sub

Private Sub Form_Load()

minElapsed% = 0
lastMinute% = 0
Time = #12:00:00 AM#

setPr = 2020
firstRun = 1
SetPressureBar.value = setPr
PressSet.Text = Str$(setPr)
volume = 0#
acceleration.Text = Str$(6#)
velocity.Text = Str$(6#)

Rem Prompt the user for an output file

Do
    CommonDialog1.FILTER = "All Files (*.*)|*.|Data Files (*.dat)!.dat"
    CommonDialog1.FilterIndex = 2
    CommonDialog1.ShowSave
    FileName = CommonDialog1.FileName

    Do While True
        If Dir(FileName) Then
            Exit Do
        Else
            FileName = InputBox("File Not Found").
            Exit Do
        End If
    Loop
    Do
        If FileLen(FileName) = 0 Then
            Exit Do
        Else
            Exit Do
        End If
    Loop
    Do
        If FileClose(FileName) = 0 Then
            Exit Do
        Else
            Exit Do
        End If
    Loop
    Do
        If FileDel(FileName) = 0 Then
            Exit Do
        Else
            Exit Do
        End If
    Loop
    Do
        If FileOpen(FileName, 2) = 0 Then
            Exit Do
        Else
            Exit Do
        End If
    Loop
End Do

ElseIf (P = Po) Then
    Rpump.Text = 0
End If

volume = volume  \(\frac{\text{distance}}{2500.5}\)
vol.Text = Left$(volume, 6)
MSComm2.InBufferCount = 0

End Sub
If (FileName = ") Then MsgBox "Error: You have to select an output file, please retry.", 48, "Error"
Loop While FileName = 

Output.Text = FileName

Rem Now open the file for output

Open FileName For Output As 

Rem Open the ClODAS08 for the RTD's

Const BoardNum = 0
Const PortNum% = AUXPORT
Const Direction% = DIGITALOUT

ULStat% = cbDeclareRevision(3.3)

ULStat% = cbErrHandling%(PRINTALL, DONTSTOP)
If ULStat% <> 0 Then Stop

Rem Open the board of the IEEE interface

Call ibfind("gpib0", b%)
If (ibsta% And EERR) Then
    Call ReportError(b%, "could not find board")
End If
Call ibrs(b%, 1)
Call ibsc(b%)

Rem Open the HP multimeter

Call ibf("hp", HP%)
If (HP% < 0) Then
    Call ReportError(HP%, "could not open HP")
End If
Rem Open the Keithley

Call ibfind("keithley", keit%)
If (keit% < 0) Then
    Call ReportError(keit%, "could not open Keithley")
End If

Call ibsre(b%, 1)

Rem Open the stepping motor

Call ibfind("stepper", stepper%)
If (stepper% < 0) Then
    Call ReportError(stepper%, "could not open stepper control")
End If

Call ibsre(b%, 1)

Rem Open the Genrad to measure the electrical conductivity

Call ibfind("genrad", genrad%)
If (genrad% < 0) Then
    Call ReportError(genrad%, "could not open Genrad")
End If

Rem Open the comm port 3 for the Left PRT reading

MSComm1.CommPort = 3
MSComm1.Settings = "9600,n,8,1"
MSComm1.InputLen = 1

Rem open the comm port 2 for the Right PRT reading

MSComm2.CommPort = 2
MSComm2.Settings = "9600,n,8,1"
MSComm2.InputLen = 1
Rem open the comm port 1 for the Block Temperature reading

    MSComm3.CommPort = 1
    MSComm3.Settings = "9600,e,7,1"
    MSComm3.InputLen = 1

End Sub

Private Sub Form_Terminate()

    Call ibsre(b%, 0)
    Call ibonl(HP%, 0)
    Call ibonl(keit%, 0)
    Call ibonl(genrad%, 0)

    Close #1

    If MSComm1.PortOpen <> False Then MSComm1.PortOpen = False
    If MSComm2.PortOpen <> False Then MSComm2.PortOpen = False
    If MSComm3.PortOpen <> False Then MSComm3.PortOpen = False

    DataValue% = 0
    ULStat% = cbDOut%(0, PortNum%, DataValue%)
    If ULStat% <> 0 Then Stop

End Sub

Private Sub SetPressureBar_Change()

    setPr = SetPressureBar.value
    PressSet.Text = Str$(setPr)

End Sub
APPENDIX B

EXAMPLE OF DETERMINATION OF METHANE GAS SOLUBILITY, AMOUNT OF HYDRATE FORMED, AND HYDRATION NUMBER
** Determination of the Solubility of Methane Gas at P=1520 Psia when the Cell Temperature cools down from state 1 (19.0°C) to state 2 (14.0°C):

In order to determine the gas solubility, the densities of the gas in both cell and pump have to be given. The temperatures in the air bath and in the cell are not the same since the insulation around the cell makes the cooling much slower than in the bath. For instance, for the ramping rate of 2.4°C/hr used in the air bath, the cooling rate will be 1.2°C/hr in the cell. Moreover, the temperature in the pump is assumed to be almost the same as the temperature in the bath, since there is no insulation on the pump cylinders.

Moreover, as seen in section C, the volume of water is 650 CC, for the upper case, and the volume of gas is 480 CC in the cell, since the total volume is 1,130 CC in the cell. For T=19.0°C, the density of water is 55.384 mole/l. Therefore, the amount of water present initially in the cell is equal to 35.9996 moles. This amount will be the total amount of water present at any time in the cell, assuming that the saturation is reached.

At T=19.0°C, the methane density is equal to 5.1801 mole/l. When the experiment starts, the temperature is the same in the bath (or pump) and in the cell. Therefore, the densities $\rho_{Cell}$ and $\rho_{Pump}$ are the same at state 1.
The amount of methane gas in the cell at state 1 is equal to:

\[
(n_{\text{Cell}})_{1} = (\rho_{\text{Cell}} \cdot V_{\text{Cell}})_{1} = (5.1801 \times 480 \times 10^{-3}) = 2.4865 \text{ moles.}
\]

The amount of methane gas in the pump at state 1 is equal to:

\[
(n_{\text{Gas}}^{\text{Pump}})_{1} = (\rho_{\text{Pump}} \cdot (V_{\text{Gas}}^{\text{Pump}} - V_{\text{Gas}}^{\text{Added Cell}}))_{1}.
\]

Therefore, \((n_{\text{Gas}}^{\text{Pump}})_{1} = (5.1801 \times (659 - 0) \times 10^{-3}) = 3.4137 \text{ moles.}\)

Thus, the total amount of methane gas in the system in the state 1 is equal to:

\[
(n_{\text{Gas}}^{\text{Total}})_{1} = (n_{\text{Gas}}^{\text{Cell}})_{1} + (n_{\text{Gas}}^{\text{Pump}})_{1} = 5.9002 \text{ moles.}
\]

At T=14°C at state 2, the methane density is equal to 5.3529 mole/l in the cell, and 5.6567 mole/l in the pump, since the temperature in the pump is already 6.20°C. Therefore, the amount of gas in the cell and in the pump are equal to:

\[
(n_{\text{Gas}}^{\text{Cell}})_{2} = (\rho_{\text{Cell}} \cdot V_{\text{Cell}})_{2} = (5.3529 \times 480 \times 10^{-3}) = 2.5694 \text{ moles.}
\]

\[
(n_{\text{Gas}}^{\text{Pump}})_{2} = (\rho_{\text{Pump}} \cdot (V_{\text{Gas}}^{\text{Pump}} - V_{\text{Gas}}^{\text{Added Cell}}))_{2}.
\]

Therefore, \((n_{\text{Gas}}^{\text{Pump}})_{2} = (5.6567 \times (659 - 70.389) \times 10^{-3}) = 3.3296 \text{ moles.}\)
Thus, the total amount of methane gas in the system, in the state 1, is equal to: 

\[(n_{Gas}^{\text{Total}})_2 = (n_{Gas}^{\text{Cell}})_2 + (n_{Gas}^{\text{Pump}})_2 = 5.8990 \text{ moles.}\]

The net amount of gas added to the liquid phase is:

\[(n_{Gas}^{\text{Net}})_1 - 2 = (n_{Gas}^{\text{Total}})_2 - (n_{Gas}^{\text{Total}})_1 = 0.0012197 \text{ moles.}\]

An extrapolation has been made from the values of Culberson and McKetta (1950) to obtain the solubility of methane gas at 19.0° C. Therefore, 

\[(n_{Gas}^{\text{Liquid}})_0 = 0.073126 \text{ moles of methane gas in pure water.}\]

The amount of methane gas added to the liquid phase at T=14° C is equal to:

\[(n_{Gas}^{\text{Liquid}})_2 = (n_{Gas}^{\text{Liquid}})_0 + (n_{Gas}^{\text{Net}})_1 - 2 = 0.074346 \text{ moles.}\]

The solubility of methane gas in pure liquid water at T=14° C is equal to:

\[x_2 = \frac{(n_{Gas}^{\text{Liquid}})_2}{[(n_{Gas}^{\text{Liquid}})_2 + (n_{Water}^{\text{Total}})]} = \frac{0.074346}{0.074346 + 35.9996} = 0.0020652.\]

The same procedure is applied until the catastrophic temperature is reached. After hydrate formation, the same procedure is followed between each state i and j until the temperature corresponding to the maximum of volume of methane gas added to the cell is reached.
** Determination of the hydration number and of the amount of hydrate formed during this experiment:

The same procedure, as explained in section E, is followed.

The theoretical hydration number:

\[ N_{th} = \frac{46}{(6 \times 0.986850) + (2 \times 0.934278)} = 5.905 \]

The solubility of methane gas in the liquid phase is equal to: \( S = 0.0021823 \).

The total number of moles of water in the cell is equal to: \( W = 35.9996 \) moles.

And the total number of moles of gas in the condensed phase after hydrate formation is equal to: \( G = 0.6050 \) moles.

Therefore, the number of moles of free water in the hydrate phase will be equal to:

\[ n_W^L = \left[ \frac{(N_{th} \cdot G - W)}{(N_{th} \cdot S - 1)} \right] = \left[ \frac{(5.905 \times 0.605) - 35.9996}{(5.905 \times 0.0021823) - 1} \right] = 32.850 \text{ moles.} \]

The number of moles of water in the hydrate phase is equal to:

\[ n_W^H = 3.149 \text{ moles. Therefore, the amount of hydrate formed is equal to:} \]

\[ \%_{Hyd} = \frac{n_W^H}{W} = 8.75. \]
The hydration number $N_{Calc}$ is equal to: \[ N_{calc} = \frac{n_W H}{G - n_G L} = 5.98. \]

**Validation of the hypotheses made:**

Let's check that the assumption of constant gas volume in the cell is verified. To prove this, the methane hydrate density at this pressure has to be calculated.

Methane gas forms a structure of type I. Therefore, the mass of water in a unit cell is equal to: \[ m_W^H = \frac{(46 \times 18.016)}{(6.022 \times 10^{23})} = 1.3766 \times 10^{-21} \text{ g.} \]

The volume of a unit cell is \( V = (1.2 \times 10^{-9})^3 = 0.1728 \times 10^{-23} \text{ l.} \)

The mass of methane in the hydrate is equal to:

\[ m_G^H = [(0.986850 \times 6) + (0.934278 \times 2)] \times \left[ \frac{16.04}{6.02 \times 10^{23}} \right]. \]

Therefore, \( m_G^H = 20.755 \times 10^{-23} \text{ g.} \)

The methane density in the hydrate phase is:

\[ \rho_G^H = \left( \frac{20.755}{16.04} + \frac{137.66}{18.016} \right) / (0.1728) = 51.707 \text{ moles/l.} \]
This value may be compared to the density of water, which is equal to 55.384 moles/l. Therefore, methane is less dense than water.

The volume occupied by the “hydrate-liquid” phase is equal to:

\[ V_{occu}^{H+L} = \left( \frac{32.850}{0.055384} \right) + \left( \frac{3.149}{0.051707} \right) = 654.0 \text{ cc.} \]

The volume occupied by the gas phase is:

\[ V_{occu}^{Gas} = (1, 130 - V_{occu}^{H+L}) = 476.0 \text{ cc.} \]

The volume assumed to be constant of 480 cc is therefore verified since the error is only 0.8%.
APPENDIX C

STATISTICAL THERMODYNAMICS OF HYDRATE EQUILIBRIA
Derived in 1959 by van der Waals and Platteuw, the statistical thermodynamics method is widely used today. The prediction method, CSMHYD from the Colorado School of Mines, is based on this method. Therefore, a brief presentation of this method is presented in this section.

**Grand Canonical Partition Function for Water**

This model is based on four assumptions:

-- The contribution of the host molecules to the free energy is independent of the occupation of the cavity, hence encaged molecules do not reshape the cavity.

-- Each cavity contains at most one guest molecule, which does not diffuse from the cavity.

-- The energy of the encaged guest molecule is independent of the number or types of other solute molecules.

-- No quantum effect are needed, which implies that classical statistics are valid.

After simplifications, the grand canonical partition function \( \Xi \) has the following expression:

\[
\Xi = \exp \left( -\frac{A^{MT}}{kT} \right) \cdot \prod_i \left( 1 + \sum_j q_{ij} \cdot \lambda_j \right)^{v_i n_w}
\]
where $A^{MT}$ is the Helmholtz free energy of empty host lattice.

$q_{J_i}$ is the partition function of a $J$ molecule in a type $i$ cavity.

$\lambda_{J}$ is the absolute chemical activity of the guest molecule $J$.

$v_{i}$ is the number of type $i$ cavities per water molecules.

(For structure 1, $v_1 = 1/23$ and $v_2 = 3/23$).

$N_W$ is the number of host molecules.

**Chemical Potential of the Solvent**

The sum of guest molecules "k" over all the cavities $i$ is related to the grand canonical partition function by:

$$N_k = \sum_i N_{k_i} = \lambda_k \cdot \left( \frac{\partial \ln \Xi}{\partial \lambda_k} \right)_{T,V,N_w,\lambda_{J=k}}$$

After simplifications, the probability $y_{k_i}$ of finding a molecule of type $k$ in a cavity of type $i$ is expressed by:

$$y_{k_i} = \frac{N_{k_i}}{v_i N_W} = \frac{q_{k_i} \lambda_k}{1 + \sum_j q_{j_i} \lambda_{j_i}}$$

The chemical potential of the solvent $\mu_W^H$ may also be expressed as a function of $\Xi$ and the following expression is obtained:
\[
\frac{\mu^H_W}{kT} = \left( \frac{\mu^M_T}{kT} - \sum_i v_i \ln \left( 1 + \sum_j q_{i,j} \lambda_j \right) \right)
\]

These two equations are very important since they allow the determination of the hydrate composition and also of the chemical potential of the hydrated water as a function of different variables, \( T, V, N_W \) or \( \lambda_i \).

Let's define a constant \( C_{k_i} \) as: \( C_{k_i} = \frac{q_{k_i} \lambda_k}{P_k} \). Therefore, the fractional filling \( y_{k_i} \) of cavity \( i \) by \( k \) molecule can be expressed as:

\[
y_{k_i} = \frac{C_{k_i} P_k}{1 + \sum_j C_{j_i} P_j}
\]

This equation is one of the most useful equation for the prediction of hydrate formation/dissociation. Moreover, this equation is similar to a Langmuir isotherm. The chemical potential of water \( \mu^H_W \) in the hydrate can be expressed as a function of the fractional occupation in the cavities:

\[
\mu^H_W = \mu^M_T + kT \sum_i v_i \ln \left( 1 - \sum_k y_{k_i} \right)
\]
This equation shows that the fractional filling of the cavities reduces the chemical potential of water in the hydrate, hence stabilizing more the hydrate. The more filling in the percentage, the value of \(1 - \sum_i y_{ki}\) will be closer to zero and the value for the chemical potential will be lower. Therefore, this will increase the stability of the hydrate.

Therefore, the CSMHYD predictions, used to determine the conditions of temperature and pressure for formation/dissociation of gas hydrates, are based on these equations. These equations are fundamental to the comprehension of thermodynamics properties of gas hydrates.
APPENDIX D

ERROR ANALYSIS
The different parameters of the hydrate formation/decomposition process, such as gas solubility, enthalpy of change, entropy change and hydration number, have an uncertainty from the sources associated with the measurements and with the calculation or approximation made.

**MEASUREMENT UNCERTAINTIES**

The measurement uncertainties are function of the accuracy and precision of the measurements made with the different apparatuses. The calorimeter measured:

-- Temperature in the air bath and in each cell,
-- Pressure in each cell,
-- Volume of gas added,
-- Electrical Conductivity Cell Resistivity,
-- Thermopile Voltage.

(1) Temperature Measurements:

The temperature measurements in each cell are made with a 500 Ohms RTD being connected to a relay which is interfaced to the computer via a digital I/O card and a Keithley 6 1/2 Digital Multimeter. Therefore, the accuracy of the measurement depends on the accuracy of the Keithley, but also on the accuracy of the Callendar-Van Dusen Equation which relates the measured resistance to the temperature. Lievois, in using a calibration method, found an uncertainty of
±0.05°C for the Callendar-Van Dusen Equation. Concerning the accuracy of the Keithley, the precision appears to be ±0.001°C. For more explanations, please refer to section 3.1 of Lievois' s Thesis. However, the temperature measurement in the bath has been modified, since a temperature controller was used and the temperature is measured via a 100 Ohms RTD. The temperature controller provides the direct measurement of the temperature in the bath, without using Callendar-Van dusen equation. Calibrated by Eurotherm Controls, the accuracy is 0.15% of the reading value. Moreover, the linearization accuracy of the RTD is ±0.05°C.

(2) Pressure Measurements:

The pressure is measured in each cell with two Heise pressure transducers, rated 10,000 Psia. The manufacturer's accuracy is ±0.07% of full range or 7 Psia. The precision for an experiment appears to be ±0.7 Psia. The transducers are interfaced to the computer via the RS232 card.

(3) Volume Measurements:

The determination of the volume of gas added is made by the difference between the volume corresponding to the displacement of the plungers to the total volume of the pump. Determined by calibration by Lievois, the total system volume is known within an error of 0.25%. The total displacement volume uncertainty appears to be ±0.01 cc or 4 × 10^{-4} % of the total volume, using standard error propagation formulas, (Crandall, in 1970, Jaech, in 1985).
(4) Electrical Conductivity Cell Resistivity:

The resistance, reciprocal of electrical conductivity, was measured with two electrodes in the conductivity cell. An alternating current is used, and the Genrad RLC multimeter measures these resistances. Therefore, the precision of the Genrad determines the accuracy of the measurement. However, the electrical conductivity resistance needed is the one at infinite frequency. Since it could not be achieved, the resistance has been measured at four different frequencies (1, 2, 4, and 10 KHz), and the infinite frequency has been determined by extrapolation. Therefore, two uncertainties are involved, the one from the Genrad and the one from the extrapolation. The best way has been to measure this uncertainty via calibration procedure. Lievois found a measurement precision of ±0.3 %, after checking measurement consistency over a period of one week.

(5) Thermopile Measurements:

The thermopile voltage did not provide a direct measurement of the heat of dissociation. The uncertainty of these measurements is not taken into account, since they were not used.

Therefore, all the uncertainties associated with the measurements are summarized in Table AX.5.
Table AX.5. Measurement Uncertainties

<table>
<thead>
<tr>
<th>Measured Parameter</th>
<th>Accuracy</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Temperature</td>
<td>±0.05°C</td>
<td>±0.001°C</td>
</tr>
<tr>
<td>Bath Temperature</td>
<td>±0.15%</td>
<td>±0.05°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>±7.0 Psia</td>
<td>±0.7 Psia</td>
</tr>
<tr>
<td>Volume</td>
<td>±0.01 cc</td>
<td>/</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cell Resistivity</td>
<td>/</td>
<td>±0.3 %</td>
</tr>
</tbody>
</table>

** CALCULATION UNCERTAINTIES

The measurements are not the only source of uncertainties. Some errors might occur from the use of empirical equations with the measured value in order to obtain the gas solubility or the enthalpy of dissociation.

(1) Density:

The densities of water and of the pure components, methane and carbon dioxide, are predicted from DDMIX, a program which calculates these data, at specific conditions of temperature and pressure. Therefore, temperature and pressure uncertainties increase the level of error for the prediction of these data. As the pressure uncertainty is the most important, the uncertainty for the prediction of these densities may be of the order of 1.0%.
(2) Solubility:

In order to obtain the solubility of methane or carbon dioxide in water, an extrapolation to low temperature is made from the literature data for higher temperatures. Results from Culberson and McKetta are used for pure methane, and report from Dodds et al. is used for pure carbon dioxide. The reading of these values may include some relatively large errors since the gas solubilities have very small values. Therefore, even if an accurate estimation of the uncertainty is not possible, an error of ±5.0% is chosen as a reasonable estimate.

(3) Enthalpy and Entropy:

The enthalpy of change and entropy change are calculated using the Clausius-Clapeyron Equation. Therefore, the slope of Ln(X) versus (1/T) will give the enthalpy of solution, and the slope of Ln(X) versus Ln(T) will give the entropy change, (X is the solubility (mole fraction) of methane or carbon dioxide in pure water). The determination of these values from the slopes includes several uncertainties, since the uncertainty on the solubility is already ±5.0%. Therefore, even if an accurate estimation of the uncertainties is not possible, the error estimated is in the order of ±10%.
(4) Hydration Number:

The hydration number is determined from the solubility values. Therefore, the uncertainty associated with the determination of the hydration number is about \( \pm 5.0\% \). Table AX.6 gives the accuracy of each parameter determined to explain the process of hydrate formation/decomposition.

**Table AX.6. Calculation Uncertainties**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>( \pm 1.0% )</td>
</tr>
<tr>
<td>Solubility</td>
<td>( \pm 5.0% )</td>
</tr>
<tr>
<td>Enthalpy-Entropy</td>
<td>( \pm 10% )</td>
</tr>
<tr>
<td>Hydration Number</td>
<td>( \pm 5.0% )</td>
</tr>
</tbody>
</table>

Therefore, all of these uncertainties play an important role in the calculation and interpretation of the heat of dissociation or amount of hydrate formed. However, even if some uncertainties appear to be important, the results obtained with the differential calorimeter are in agreement with the literature and reflect the process of hydrate formation/decomposition.