

**Gas Hydrate Formation Kinetics Measurement of Mixed Carbon
dioxide and Methane**

by
Syed Osama Bukhari

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2013

Universiti Teknologi PETRONAS
Bander Seri Iskander
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

**Gas Hydrate Formation Kinetics Measurement of Mixed Carbon dioxide and
Methane**

by

Syed Osama Bukhari

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Azizul Buang)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SYED OSAMA BUKHARI

ABSTRACT

A new technique which uses gas hydrate formation to capture carbon dioxide from natural gas is believed to have a good future prospect. However, in developing such hydrate based technology, an understanding of kinetics of hydrate formation is essential for process designing. Given that the modelling efforts have not been completely successful in describing the hydrate growth kinetics, currently we may rely on experimental data for this purpose. However at present there is only a limited number of hydrate growth kinetics data available in the literature especially for the hydrates of mixed methane and carbon dioxide. In this study, we report the values of induction time and growth rate constant for hydrates of mixed methane and carbon dioxide using their two different compositions. The two experiments have been conducted under similar conditions. The results are used to discuss the effect of gas composition on the kinetics of hydrate formation.

ACKNOWLEDGEMENTS

The author would like to thank and acknowledge the contributions of Dr. Azizul Buang, Dr. Khalik Sabil, Mr. Behzaad Partoon, Ms Nurmala, Mr. Qazi Nasir and Mr. Khan. All their support, time and assistance in the completion of this project is much appreciated.

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	i
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	2
1.3 Objectives.....	2
1.4 Scope of Study	2
CHAPTER 2 LITERATURE REVIEW & THEORY.....	4
CHAPTER 3 METHODOLOGY	10
3.1 Project Activities.....	10
3.2 Hydrate Incipient line.....	10
3.3 Gas Mixing.....	11
3.4 Experimental Apparatus & Procedure	12
3.5 Gantt Chart and Key Milestones	15
CHAPTER 4 RESULTS & DISCUSSION	16
4.1 Hydrate Incipient (equilibrium) Line Prediction by CSMGem	16
4.2 Gas Mixing and Gas Chromatography (GC) Results.....	17
4.2.1 Gas Chromatography (GC) Analyzer Calibration.....	18
4.3 Experiment Results	19
4.3.1 Experiment 1	19
4.3.2 Experiment 2	22
CHAPTER 5 CONCLUSION AND RECOMMENDATION.....	25
REFERENCES.....	26
APPENDIX 1 MATLAB Formula for Z	27
APPENDIX 2 Open Literature.....	28

LIST OF FIGURES

		Page
Figure 2.1	Schematic Representation of Phase Equilibrium of Water in a (P-T) Diagram	9
Figure 3.1	Schematic Representation of the High Pressure Kinetics Measurement Apparatus	12
Figure 4.1	Hydrate Three-Phase (H-L _w -V) Equilibria Lines	16
Figure 4.2	Experiment 1 Pressure/Temperature vs. Time Plot	19
Figure 4.3	Experiment 1 Hydrate Growth Trend	20
Figure 4.4	Gas Moles Consumption Trend for Experiment 1	20
Figure 4.5	Rate Constant for Experiment 1	21
Figure 4.6	Experiment 2 Pressure/Temperature vs. Time Plot	22
Figure 4.7	Experiment 2 Hydrate Growth Trend	23
Figure 4.8	Gas Moles Consumption Trend for Experiment 2	23
Figure 4.9	Rate Constant for Experiment 2	24

LIST OF TABLES

		Page
Table 2.1	Application of Gibb's phase rule in a P-T diagram of a unary water system	8
Table 3.1	Gas Mixtures Compositions for Experiments	12
Table 4.1	Gas Chromatography Analysis Results	17
Table 4.2	GC Calibration	18

CHAPTER 1

INTRODUCTION

1.1 Background

A Gas hydrate is a crystalline solid made-up of a cage of water molecules inside which there is a gas molecule being trapped. Gas hydrates are ice-like crystalline compounds that naturally exist in huge quantities on earth especially in permafrost and sea floor. Gas hydrates form different crystal structures (sl, sll or H) with a variety of gases. Hence there are various types of gas hydrates formed by different gases including methane, ethane, carbon dioxide and nitrogen.

There has been growing interest in studies of gas hydrates by researchers for several reasons. Some of the most popular areas of hydrate research are discussed here. Firstly, gas hydrates are seen as a promising energy resource for the future after the discovery of their vast natural reserves on earth. Secondly, gas hydrates are encountered as a problem in the petroleum industry where they can form inside transport gas pipelines often resulting in pipeline blockages. Finally, gas hydrates can be used in developing new technologies for carbon dioxide capture and sequestration. A technique for separating carbon dioxide gas from natural gas is currently under study (Sabil, 2009).

The principle of gas separation by hydrate formation process is simple. Because of the difference in chemical affinity between CO₂ and CH₄ in the hydrate structure, when hydrate crystals are formed from a mixture of these two gases, CO₂ concentration might be enriched in the hydrate phase while CH₄ would be reduced in the hydrate and increased in the gas phase at equilibrium. The hydrate phase is then dissociated by depressurization or/and heating and CO₂ can be recovered as a separated gas (Belandria, 2010). However such application of hydrate technology requires the development of effective hydrate formation reactors, which, in turn relies on a comprehensive understanding of the hydrate formation kinetics. Contrary to hydrate thermodynamics, hydrate kinetics are still poorly understood because handful of studies have been completed in this area (Cláudio, 2008).

Gas hydrate formation kinetics is a challenging area in gas hydrate research. This is because time-dependent properties of hydrates are difficult to measure. A model for hydrate growth process by Engleroz-Bishnoi is already available since 1987 but it cannot be completely relied upon due to some of its limitations. As described by Sloan & Koh (2008) “Although significant advances have been achieved in measurement and modelling of hydrate formation, there are still significant knowledge gaps in this area to be filled before a reliable transient hydrate growth model can be developed”.

Essentially, kinetics is concerned with the rate at which the phase transformation or hydrate formation occurs. The rate of nucleation, e.g. number of hydrate crystal nuclei formed per unit time per unit volume is an extremely difficult measurement and to date there are no data reported. However, fortunately the rate of hydrate crystal growth can be defined experimentally. According to Linga (2007), we can actually describe hydrate growth by determining the rate of gas uptake during hydrate formation. It enables us to find the growth rate constant and also the induction time for hydrate formation.

1.2 Problem Statement

Further development in gas hydrate technology for CO₂ separation from natural gas essentially requires the availability of hydrate formation kinetics data. However at present there is only a limited number of data available in the literature especially for the hydrates of mixed methane and carbon dioxide.

1.3 Objectives

To obtain the formation kinetics data of gas hydrates formed by using two different composition mixtures of methane and carbon dioxide gases. The kinetics data includes the induction time and growth rate of hydrate formation.

1.4 Scope of Study

This study required thorough literature review from journal articles, conference papers as well as academic books on topics especially related to the formation kinetics and phase behavior of gas hydrates.

Mainly experimental work was required to fulfill the objective of this study. Apart from that, simulation was done by using CSMGem modeling program to predict hydrate incipient lines and gas chromatography was performed to check gas mixture composition at different times.

CHAPTER 2

LITERATURE REVIEW & THEORY

Research in kinetics of hydrate formation was initiated by the USSR in the mid 1960's. This research effort had begun in view of the potential of natural gas hydrates as a substantial energy resource for the future.

Today, kinetics of hydrate formation has become a popular area of hydrate research especially in the petroleum industry. This is because hydrate technology in oil/gas flow lines is crucial for solving the problem of flow assurance in pipelines. Lately, engineers had been trying to avoid hydrate formation in pipelines from happening at all. But now the solutions for flow assurance are shifting from hydrate avoidance to risk management due to economic considerations. There can be ways to inhibit hydrate growth without affecting the flow in pipelines but economically it is still not very satisfying. Hence, in order to develop this technology further and find economically more attractive methods for flow assurance, a greater understanding of the hydrate formation kinetics is required.

It is believe that soon the hydrate formation kinetics studies would also be useful in assessment and production of energy from vast natural reserves of hydrates in permafrost and oceanic deposits (Sloan & Koh, 2008, p.17). Furthermore, these studies would greatly help us in developing new technologies for separating carbon dioxide from industrial gases through the formation of carbon dioxide hydrates (Sabil, 2009).

However, researchers have had been facing several challenges in studies of hydrate formation kinetics. One of the current challenges is to model the hydrate growth process. An attempt to correlate the hydrate growth process with their intrinsic (natural) growth kinetics was first presented in the Engleroz-Bishnoi model in 1987 but this model cannot be completely accepted due to some of its limitations. (Sloan & Koh, 2008, p.169).

In their critique for the Engleroz-Bishnoi model, Sloan & Koh (2008) have indicated some limitations for modeling the hydrate growth process. These

limitations are briefly explained here. Firstly, any kinetic model has to be used with caution because hydrate nucleation (initiation of growth, occurring during the induction period) is a stochastic (random) process with significant scatter in the data at low driving force under isothermal conditions. Secondly, every model for hydrate formation may be apparatus-dependent, making it doubtful to be applied in actual systems such as natural gas pipelines. And finally, a model based on a particular crystal structure; sI or sII may not be a good representation of other crystal structures such as H.

The hydrate nucleation process refers to the formation and growth of hydrate nuclei to a critical size (Sabil, 2009). Current hypothesis for hydrate nucleation are based upon the better-known phenomena of water-freezing, the dissolution of hydrocarbon in water and computer simulations of both phenomena. Evidence from experiments show that nucleation is a statistically probable process; stochastic. Hence hydrate induction times (the time elapsed before the hydrates begin to form in the system) are stochastic as well, with limited predictability for hydrate onset, particularly at low driving forces, and tend to be apparatus-dependent (Sloan & Koh, 2008, p.116).

According to Sloan & Koh (2008)

Recent statistical measurements performed by Wilson et al (2003, 2005) suggests that the freezing temperature for hydrate/ice nucleation varies only within around 2°C at high driving forces under continuous cooling. In essence, there is only a limited number of statistical data available in the literature, with varying reports of the extent of reproducibility of induction times from different groups. Statistical analyses are required in order for reliable induction times to be obtained for gas hydrate systems. To date, statistical analyses of hydrate induction time measurements needs to be performed and correlated between different apparatus setups. In order to assess whether the induction time-freezing temperature of gas hydrates can be predicted to an acceptable level of accuracy, much work still remains to be performed. (p.142)

Sloan & Koh (2008) also points out that “after the stochastic nature of hydrate crystal nucleation, the quantification of the hydrate growth rate or growth kinetics provides some relief for modeling hydrate formation. However, only a limited amount of accurate data exists for the crystal growth rate after nucleation”. The hydrate growth process refers to the growth of stable hydrate nuclei as solid hydrates (Sabil, 2009). Some of the available sources of data on measurements of hydrate growth rates are listed in the appendix.

The closed loop (T-cycle) method used by Ohgaki et al. [1993] can be used for the measurement of formation kinetics of hydrates. However before proceeding to the kinetic measurement, we have to predict the phase equilibria conditions under which the hydrates can form. Fortunately, the field of phase equilibria thermodynamics of hydrates has now become well established. The usual protocol in experimentally obtaining phase equilibria data involves using the Cailletet apparatus or observing the hydrate phase by direct means, such as an associated pressure decrease or temperature increase in the fluid phase. However, with the availability of modelling programs like hydraFLASH and CSMGem, it has become much easier to predict the phase equilibria conditions of hydrate to an acceptable level of accuracy.

According to Sloan & Koh (2008)

Villard was the first to determine hydrates of methane, ethane (1888), and propane (1890), but he was not successful in the formation of nitrogen hydrates. In order to form methane and ethane hydrates, he replaced the glass container of the Cailletet with a round metal jar, and formed hydrates of methane at 26.9 MPa and 293.4 K. Models of the Cailletet apparatus are in current use at the Technical University of Delft, Netherlands (Peters et al., 1933; Jager et al., 1999) (p.327).

Experimentalists of hydrates have proved three important principles to guide the development of apparatuses and methods to form hydrates. These principles are:

1. Vigorous agitation is necessary for complete water transformation.
2. Hydrate dissociation is used to measure the hydrate equilibrium point.

3. A rapid decrease in pressure or an increase in temperature indicates hydrate formation in a constant volume apparatus.

Generally, stirred autoclave cells with P, T control are used for hydrate phase equilibria measurements. However over the last 50 years, hydrate phase equilibria apparatus have been developed with the above three principles. In an isochoric operation, the temperature of the cell is lowered from the vapor-liquid region, and isochoric cooling of the gas and liquid causes the pressure to decrease slightly. Hydrates form at the metastability limit, causing a marked pressure decrease, ending at the three phases (L_w-H-V) pressure and temperature. The temperature is then slowly increased to dissociate the hydrates. On a pressure –temperature plot, the hydrate dissociation point (or hydrate equilibrium point) is taken as the intersection of the hydrate dissociation trace with the initial cooling trace. This procedure is commonly used for high pressure hydrate formation, and provides an alternative to visual observation which is the primary option in Cailletet apparatus (Sloan & Koh, 2008, p.328-331).

Recently, Tohidi and coworkers (Burgass et al., 2002; Mohammadi et al., 2003) have applied a novel method for measuring gas hydrate phase equilibria (L_w-H-V), which is based on a Quartz Crystal Microbalance (QCM) (Sloan & Koh, 2008, pg.332).

Furthermore, some phase equilibria data for binary-guest mixtures containing methane and carbon dioxide has been obtained by few researchers in the past. A chronological listing of this data is provided in the appendix.

For understanding the concept of phase equilibria of hydrates, the phase diagrams are very useful. These diagrams can also define the boundaries for a hydrate forming region. However, the construction of phase diagrams rests on experimental data for phase boundaries, and on the Gibb's phase rule. The diagrams use symbols of I, L_w, H, V and L_{HC} to represent ice, liquid water, hydrate, vapour, and liquid hydrocarbon respectively.

By the Gibb's phase rule, an equilibrium state of a system with (N) components and (π) phases can be fully described by $2 + \pi(N-1)$ intensive variables namely P (Pressure), T (Temperature) and etc. Hence the number of degrees of freedom, F, is the difference between the number of variables and the number of equilibrium conditions, $F = N - \pi + 2$ (Sabil, 2009).

A unary (single component) system has the simplest phase diagram. Hence for the ease of explanation, an example of applying the Gibb's phase rule for a unary system of water is given in Table 2.1.

Table 2.1 Application of Gibb's phase rule in a P-T diagram of a unary water system
[Adapted from Sabil, 2009]

π	\emptyset	Example	F	Representation in P-T plane
1	0	I, L, V	2	region, surface
2	0	I-L, I-V, L-V	1	line (curve)
1	2	L=V	0	point
3	0	I-L-V	0	point

The phases that can occur in a unary water system are solid/ice (I), liquid (L_w) and vapour (V). Each equilibrium line shown in Figure 2.1 below represents a phase boundary and gives the conditions at which two phases may coexist at equilibrium. The intersection of these lines represents the triple point, i.e. the conditions where liquid water, gaseous water and ice coexist in equilibrium. Since the number of degrees of freedom is equal to 0 at these conditions, the triple point can only occur at a unique temperature and pressure value, T_{tr} and P_{tr} respectively. A critical point occurs at the end of an equilibrium line where the properties of the two phases become indistinguishable from each other. In the case of the unary water system, the critical point is located at the end of the liquid-vapour line at unique temperature and pressure values of T_c and P_c respectively.

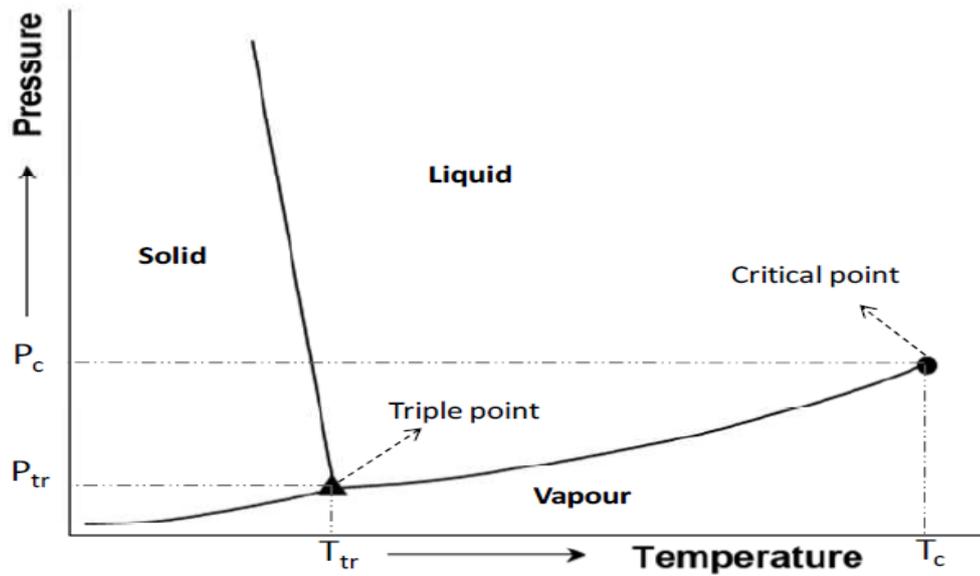


Figure 2.1 Schematic Representation of Phase Equilibrium of Water in a (P-T) Diagram [adapted from Mooijer-van den Heuvel, 2004]

However, in this project the hydrate system is ternary with water, methane and carbon dioxide gas being the system constituents. In such ternary system, the maximum number of degrees of freedom is greater than or equal to four. Hence the representation of the complete phase equilibrium requires four or more variables to be defined. Often, this is not feasible to work with. However, if the composition of each component is fixed, then the phase behaviour at this fixed composition can be depicted in a P-T diagram.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

The project mainly involves experiments to measure the formation kinetics of hydrates formed from a mixture of methane and carbon dioxide gases. The results of this study will be used to determine the effect of variations in methane and carbon dioxide gas mixture composition on the induction time and growth rate of hydrate formation. Precisely, the following main activities are included in the project:

- Prediction of hydrate incipient line by CSMGem modelling program
- Obtaining gas mixture of the required composition by using a gas mixing station and analyzing gas mixtures by gas chromatography (GC) to confirm their composition.
- Monitoring and recording experimental data by a data acquisition system
- Analysis of data to find induction time and calculate growth rate constant
- Analysis of results to understand the effect of variations in methane and carbon dioxide gas mixture composition on the induction time and growth rate of hydrate formation.

3.2 Hydrate Incipient line

The hydrate incipient lines were predicted for different gas mixtures of methane and carbon dioxide. Predictions were made by using CSMGem modelling program. This program is built on a thermodynamic model capable of predicting hydrate phase behaviour, including phase boundaries and flash calculations. It performs any selected calculation on our choice of components and conditions. In this case the program calculated the required pressure for hydrate formation at a specified temperature. The calculated values of pressure over a range of temperature formed the hydrate incipient line. This line enables us to identify the temperature and pressure (phase equilibrium) conditions which separates the hydrate forming and non-forming regions. By knowing the boundary of the hydrate forming region, we can set the appropriate experimental conditions required to form the hydrate. Another advantage of having hydrate incipient line is that the onset of nucleation process or

induction time can be easily approximated by knowing the moment when the system crossed the line and entered into the hydrate forming region. It is assumed that the hydrate nucleation process would begin at the time when the phase equilibrium conditions in the system have reached the hydrate forming region. During the induction time period, the temperature and pressure in the system are expected to be stable until the hydrate appears to start forming at the turbidity point. Turbidity point is characterized by a rapid drop in pressure and an associated rise in temperature, this marks the completion of the hydrate nucleation process and the beginning of the hydrate growth process.

3.3 Gas Mixing

A gas mixing system was used to mix appropriate amounts CO₂ and CH₄ gases in order to obtain a required gas mixture composition.

Following are some of the main steps involved in operating the gas mixing system:

1. The vacuum pump is run to empty the tanks and gas flow lines.
2. The required mass flow of both the gases in (mg/min) and pressure in (bars) are set on the control panel
3. The booster pumps then starts to pump the gas mixture into the reactor until the set pressure is achieved.
4. Gas sample is obtained from the sampling tank for analysis by Gas chromatography to confirm the gas composition

The system has flow meters to control the mass flow of gases. It also has a mixing tank and booster pump which delivers the gas into the reactor. The pump starts automatically when a new pressure value is set and it also stops automatically as soon as the reactor pressure achieves the set value.

3.4 Experimental Apparatus & Procedure

The project involves two experiments, each experiment using a different gas mixture composition. Table 3.1 below lists the gas mixtures used in these experiments.

Table 3.1 Gas Mixtures Compositions for Experiments

Experiment	Gas Mixture Composition	
	CH ₄ (mol %)	CO ₂ (mol %)
1	5	95
2	65.4	34.6

Figure 3.1 shows a schematic representation of the high pressure apparatus used to run all the experiments. The apparatus consists of a high pressure stainless steel vessel with an internal volume of 500ml. The maximum working pressure for the vessel is 300 MPa. The vessel is immersed in a water bath to keep the temperature constant at a desired value. The temperature inside the vessel is monitored both in the gas phase and in the liquid phase by two thermocouples with an accuracy of $\pm 0.1^\circ\text{C}$. To achieve proper mixing in the liquid sample, a magnetic stirrer is placed in the vessel. The pressure inside the cell is measured with a pressure transducer. The pressure and temperature and time readings are recorded and stored in a data acquisition system.

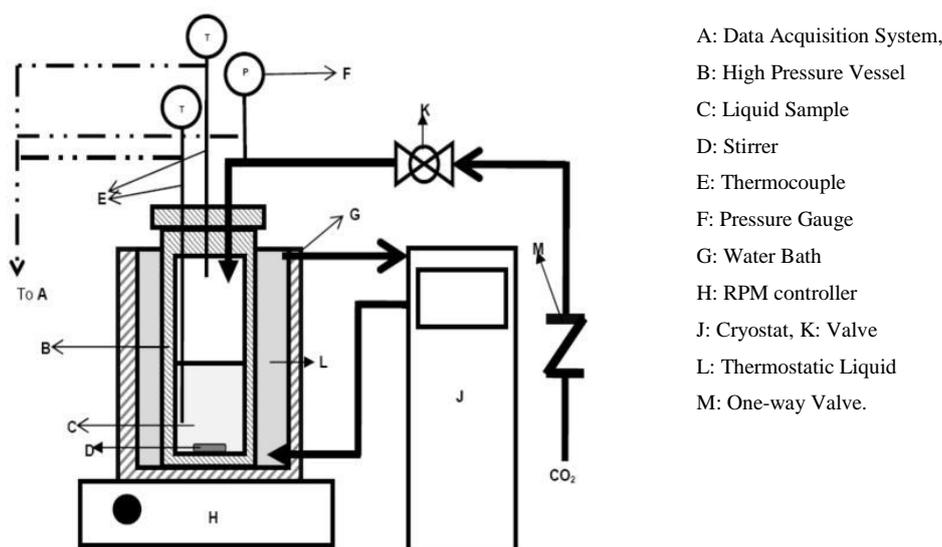


Figure 3.1: Schematic Representation of the High Pressure Kinetics Measurement Apparatus [adapted from Sabil, 2009]

To begin with the experiment, the vessel is first filled with 100ml of deionised water. Any air present in the vessel is flushed out by purging it five times with the prepared gas mixture. The vessel is then filled with the gas mixture up to the desired pressure and its temperature is controlled by using the water bath. At this point the temperature and pressure values should lie outside the predicted hydrate forming region for that particular gas mixture. Once the desired temperature and pressure are stabilized (typically within 2 min) the stirrer in the vessel is set at 500rpm. We should now notice a decrease in pressure since the dissolution of gas in water is promoted by the stirring effect. After the pressure and temperature have stabilized, we then start to slowly reduce the temperature down to 273K. This is time zero for induction time. The induction time which is the time taken before the hydrate begins to form in the system can be obtained by observing the pressure- time relationship. A rapid decrease in pressure or an increase in temperature indicates hydrate formation in the system. Hence during the experiments, changes in pressure and temperature should be recorded every second by a data acquisition system. When the pressure and temperature of the system remains unchanged for 2 to 3 hours, this indicates that hydrate formation is completed and the experiment is ended. Beyond the induction time, massive hydrate growth process is studied through the measurement of gas consumption and the calculation of apparent rate constant. The key to obtaining meaningful results is an accurate measurement of the amount of gas consumed and the control of the mixing conditions in the vessel. The first requirement is satisfied through accurate pressure measurements. The second requirement is satisfied through the magnetic stirrer. Finally, by obtaining the number of moles of gas(s) consumed over time, we calculate the rate constant for hydrate formation (Linga, 2007).

Calculation of number of moles consumed

Adapting the closed loop (T-cycle) method by Ohgaki et al.[1993], the equation of state for real gases is used to calculate the moles of gas consumed. The equation is described as below:

$$PV = nZRT \tag{1}$$

This can be rearranged as,

$$n = PV/ZRT \tag{2}$$

The compressibility factor, Z is calculated from the Peng-Robinson Equation of State. To solve for the values of Z, a MATLAB program can be used. The coding for this program has been included in the appendix.

$$Z^3 - (1-B) Z^2 + [A-3B^2 - 2B] Z - (AB-B^2-B^3) = 0 \quad (3)$$

Where a (T), A, B and b are defined as:

$$b = 0.7780RT_c/P_c \quad (4)$$

$$a(T) = [0.45724 (R^2 T_c^2) / P_c] [1 + \beta (1 - (T/T_c)^{1/2})] \quad (5)$$

$$\beta = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad (6)$$

Where T_c is the critical temperature, P_c is the critical pressure and ω is the acentric factor of the gas.

The Peng-Robinson equation is intended for description of the PVT behavior of pure compounds. However, it can also be used for mixtures of compounds by using "mixture-averaged" values for the equation parameters. Let the values of parameters $a_{ii}(T)$ and b_i be the pure-component values of $a(T)$ and b , respectively, for the i^{th} compound in a mixture. Also, let y_i be the mole fraction of component i in the mixture. Then mixing rules are applied to compute the mixture-averaged values of $a(T)$ and b for a mixture of n different compounds as follows:

$$b = \sum_{i=1}^n y_i b_i \quad (7)$$

$$a(T) = \sum_{i=1}^n y_i \sum_{j=1}^n y_j a_{ij} \quad (8)$$

Where $a_{ij} = a_{ji} = (a_{ii} a_{jj})^{0.5}$

$$\text{Gas moles consumed} = n_0 - n \quad (9)$$

Where,

n_0 = initial number of moles of gas at turbidity point

n = number of moles of gas at time t

It is assumed that gas moles are the combined moles of CO₂ and CH₄ gases together.

$$\text{Gas concentration} = C = P/RTZ \quad (10)$$

Calculation of rate constant

Pressure independency is assumed for calculation of hydration rate like in [Ohgaki et. al, 1993]. It is also assumed that the hydrate formation is a first-order reaction. In this case, the apparent rate constant can be calculated as:

$$\frac{dC_h}{dt} = k (C - C_s) \quad (11)$$

Where;

C_s = Saturated concentration of the gas at the stationary point (mol/L)

C_h = C = Concentration of gas in hydrate at time t (mol/L)

k = Apparent rate constant (1/sec)

t = time (sec)

The rate constant k can be found by plotting a graph of $\ln((C_0 - C_s)/(C - C_s))$ vs. time. We then plot a line of best fit and calculate its gradient. The value of rate constant k (M/s) is equal to the slope of this line.

3.5 Gantt Chart and Key Milestones

Activities	2012							
	Aug	Jan	Apr	Aug	Nov	Feb	May	Aug
Registration								
Literature review and fundamental study								
Development of research proposal defense								
To obtain phase equilibria data using CSMGem								
Kinetic measurements for CO ₂ – CH ₄ hydrates								
Paper works and Dissertation								

Key Milestone:

- Hydrate Incipient Line Prediction by CSMGem.
- Obtaining formation kinetic data through experimentation.
- Analysis of kinetic data.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Hydrate Incipient (equilibrium) Line Prediction by CSMGem

Hydrate incipient lines predicted by CSMGem for different compositions of gas mixtures are displayed in figure 4.1. Each line shows 3-phase equilibrium between H- Hydrate, L_w- Liquid water and V-Vapor phases. In all the equilibrium calculations by CSMGem, the mole fraction of water used is 70% and the mole fraction of the gas is 30%. The components in the gas phase are only methane and carbon dioxide. Hence a gas mixture for instance 5% methane would contain 95% carbon dioxide as the remaining gas constituent.

To ensure that hydrates do not form while settings up the experiment, an experiment must be started from a point outside the hydrate forming region. The selected initial conditions for the experiments in this study are a temperature of 288K and pressure of 100bars. After setting up these initial conditions inside the vessel, the temperature is then slowly reduced to smoothly enter into the hydrate forming region which lies above each hydrate incipient line.

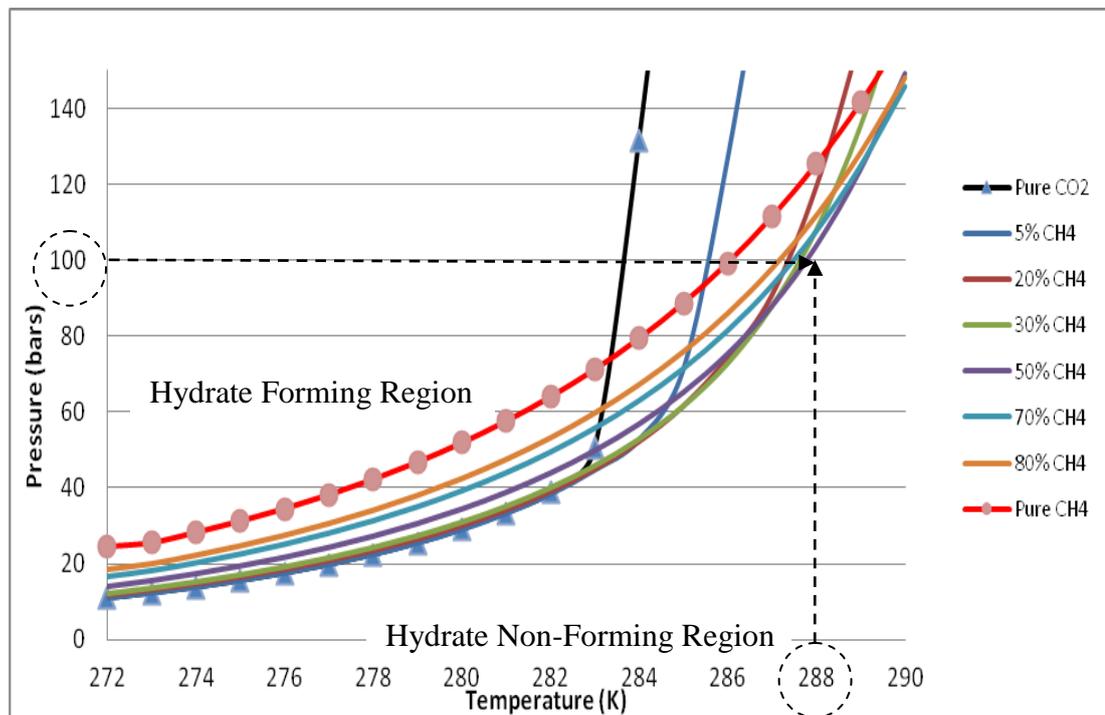


Figure 4.1: Hydrate Three-Phase (H-L_w-V) Equilibria Lines

4.2 Gas Mixing and Gas Chromatography (GC) Results

A gas mixing unit was used to prepare gas mixtures for the experiments. Carbon dioxide and methane gases were mixed in a cylindrical tank of the gas mixing unit. This mixture was then sent into the reactor by a compressor installed in the mixing unit. The amount of gases to be mixed was calculated based on the required mole ratio for gases and their relative molar mass. This calculation was then used to set the flow rates of both the gases in mg/min. For example to form a gas mixture of 30% CH₄ and 70% CO₂, flow rates of 300mg/min CH₄ and 1925mg/min CO₂ can be used. A pressure of 100bar was set for the reactor so that the compressor can operate until the pressure inside the reactor was reached at 100bars.

Each gas mixture was immediately collected in a tedlar sampling bag and sent for analysis with GC. The results from GC were used to confirm the composition of the gas mixture formed by the mixing unit and also to find the relative amounts of gases in equilibrium with the hydrate. Hence two gas samples were collected for each experiment, one before hydrate formation and one after hydrate formation. A gas sample before hydrate formation help us to confirm the actual composition of gas that was sent into the reactor to form the hydrate. And a gas sample after hydrate formation indicates the changes in gas mixture composition after the hydrate formation.

Table 4.1: Gas Chromatography Analysis Results

Experiment 1	Methane	Carbon dioxide
Mole fraction (%)	5	95
mmol	2	38
Flow rate (mg/min)	32	1672
GC before hydrate	5.23	94.77
Error (%)	4.6	0.24
GC after hydrate	13.2	86.8

Experiment 2	Methane	Carbon dioxide
Mole fraction (%)	65.40	34.60
mmol	41.25	21.82
Flow rate (mg/min)	660	960
GC conc. before hydrate	66.99	33.01
Error (%)	2.4	4.8
GC conc. after hydrate	69.7	30.3

4.2.1 Gas Chromatography (GC) Analyzer Calibration

GC calibration was performed with samples of 99.95 % pure methane gas and 99.99% pure carbon dioxide gas. The calibration was performed by using the calibration curve method. After the calibration, 2 standard gas mixture samples were tested to check for errors (%). The results of these tests are satisfactory, as provided in table 4.2.

Table 4.2: GC Calibration

Standard sample		Methane	Carbon dioxide
1	mole fraction (%)	30	70
	GC concentration Result	30.388	69.612
	Error (%)	1.29	0.55
2	mole fraction (%)	28	72
	GC concentration Result	28.039	71.961
	Error (%)	0.14	0.05

4.3 Experiment Results

4.3.1 Experiment 1

The pressure and temperature vs. time graphs obtained for experiment 1 are displayed in figure 4.2 below.

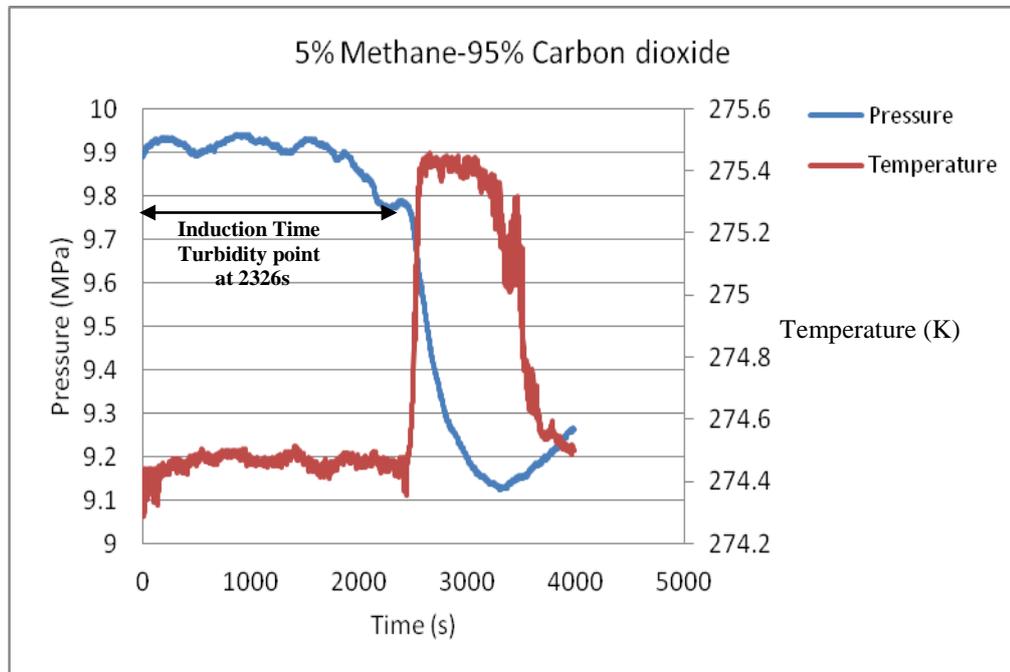


Figure 4.2: Experiment 1 Pressure/Temperature vs. Time Plot

Figure 4.2 above shows that both pressure and temperature were stable until 2326 seconds after which a rapid drop in pressure and simultaneous rise in temperature occurred. This rapid drop in pressure occurs due to the entrapment of gas molecules in the hydrate structure which decreases their amount in the gas phase and subsequently decreases the overall gas pressure in the vessel. The rise in temperature occurs since hydrate formation is an exothermic process. At the start of this experiment the pressure was at 10Mpa and temperature at 288K. The temperature was then slowly reduced down to 274.4K which also resulted in a decrease in pressure down to 9.9MPa due to gas contraction. This point is recorded as time zero in the graph. The time period from between zero to 2326s is the induction time for this experiment which is around 38.8min. This time indicates the turbidity point where massive hydrate growth starts.

Growth Rate and Moles Consumption

A closer view of hydrate formation graph during massive hydrate growth is shown in figure 4.3. The section of graph which is selected to calculate for the mole of gas consumed is from 2320s to 3320s. This section is indicated with a dotted oval in the figure 4.3.

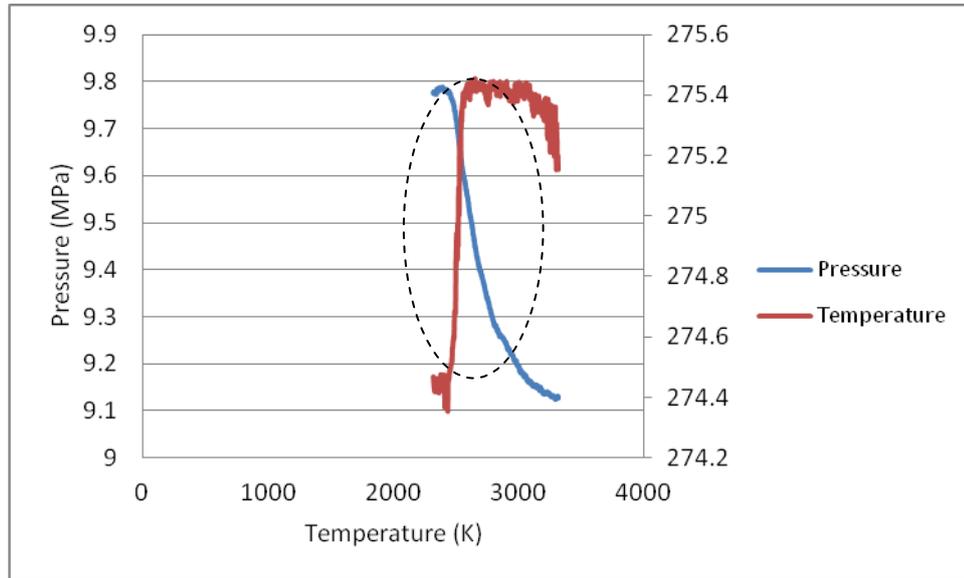


Figure 4.3: Massive Hydrate Growth Trend

Now a trend for gas mixture moles consumed during massive hydrate growth is shown in figure 4.4 below. The mole consumption calculation is based on the number of initial gas moles at 2320s.

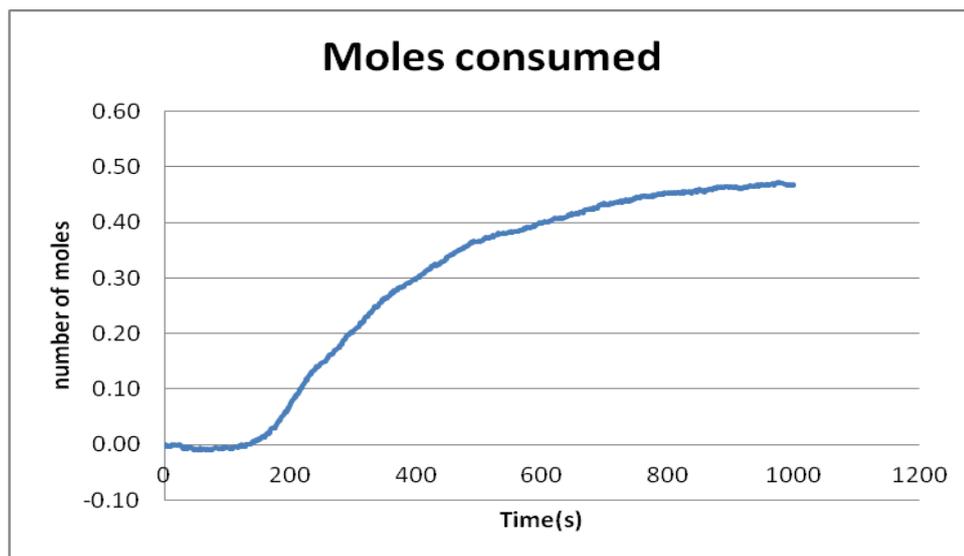


Figure 4.4: Moles Consumption for Experiment 1

It can be observed that the mole consumption gradually increases over time reaching a roughly constant maximum value between 0.4 – 0.5 moles/s.

Rate Constant

The rate constant for experiment 1 is estimated from the plot in figure 4.5 below. The slope of the regression line gives the value of the rate constant. In this case the value is $k = 0.0056$ per second.

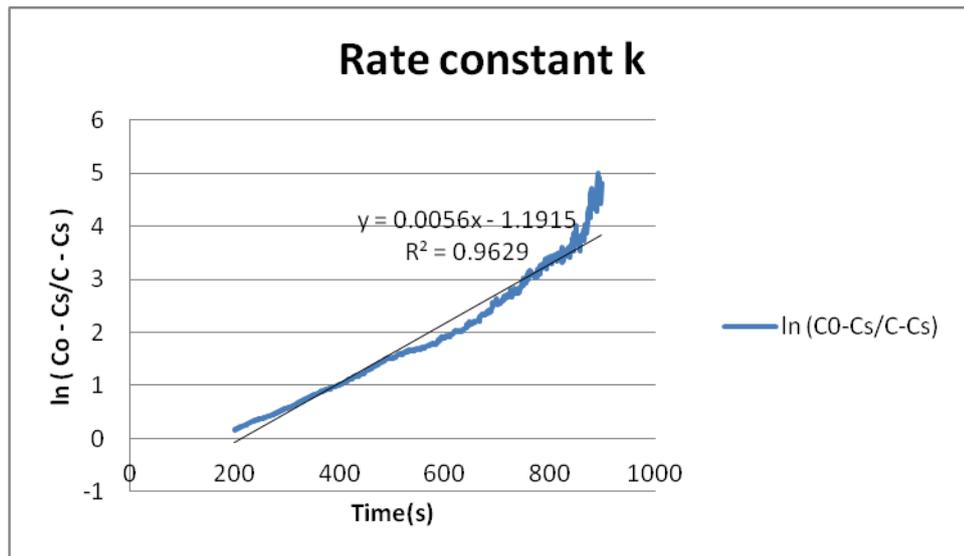


Figure 4.5: Rate constant for Experiment 1

Hence the value of growth rate constant for experiment 1 is 0.0056 per second.

4.3.2 Experiment 2

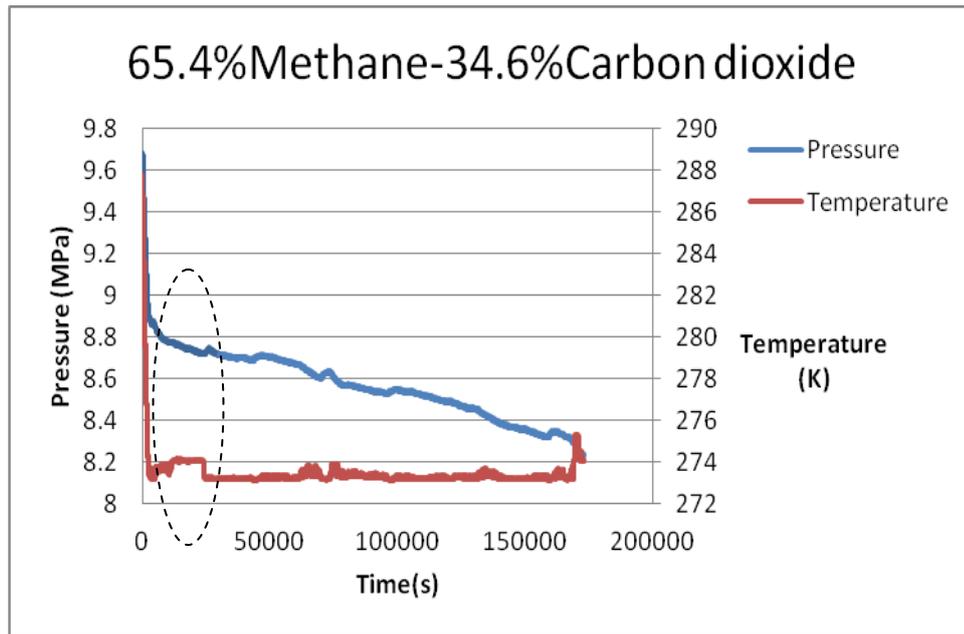


Figure 4.6: Experiment 2 Pressure/Temperature vs. Time Plot

Likewise experiment 1, the same procedure was adapted to find growth rate constant and induction time for experiment 2. The hydrate growth region is indicated by the dotted oval in figure 4.6 above. For this region the value of hydrate formation rate constant is calculated as $k = 0.0001$ per second. And the induction time is found to be around 97.4 min.

Hence experiment 2 with a higher CH_4 content showed even slower rate of hydrate formation and longer induction time as compared to experiment 1 with a higher CO_2 content. Further drop in pressure without any rise in temperature indicates towards gas dissolution in the water. However regions where we see a drop in pressure accompanied with rise in temperature indicate times during which hydrate growth occurs. The rise in temperature occurs since hydrate formation is an exothermic process.

Growth Rate and Moles Consumption

A closer view of hydrate formation graph during massive hydrate growth is shown in figure 4.7. The section of graph which is selected to calculate for the mole of gas consumed is from 5846s to 25846s. This section is indicated with a dotted oval.

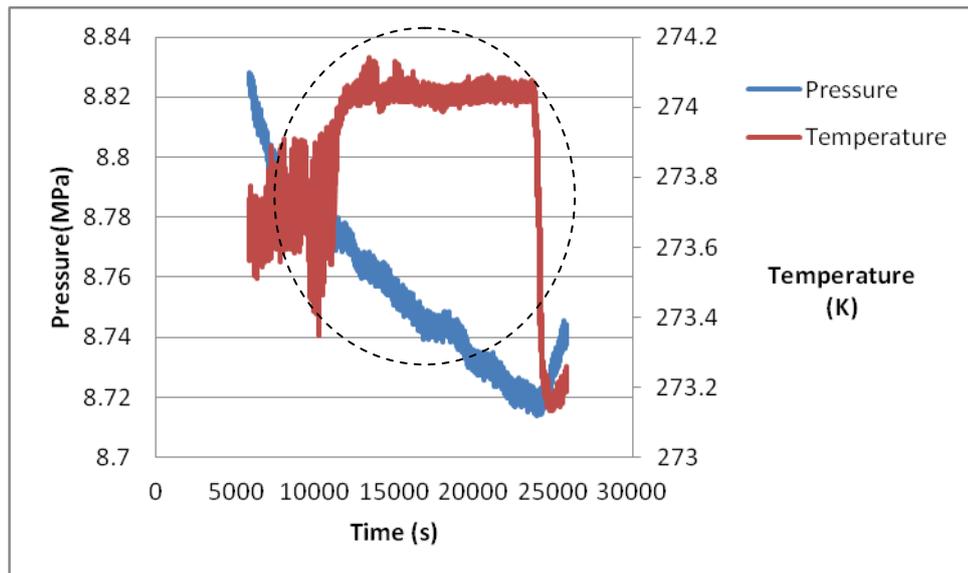


Figure 4.7: Experiment 2 Hydrate Growth Trend

Now a trend for gas mixture moles consumed during massive hydrate growth is shown in figure 4.8 below. The mole consumption calculation is based on the number of initial gas moles at 5846s. It should be noted that 5846s is assumed as time zero in the graph below.

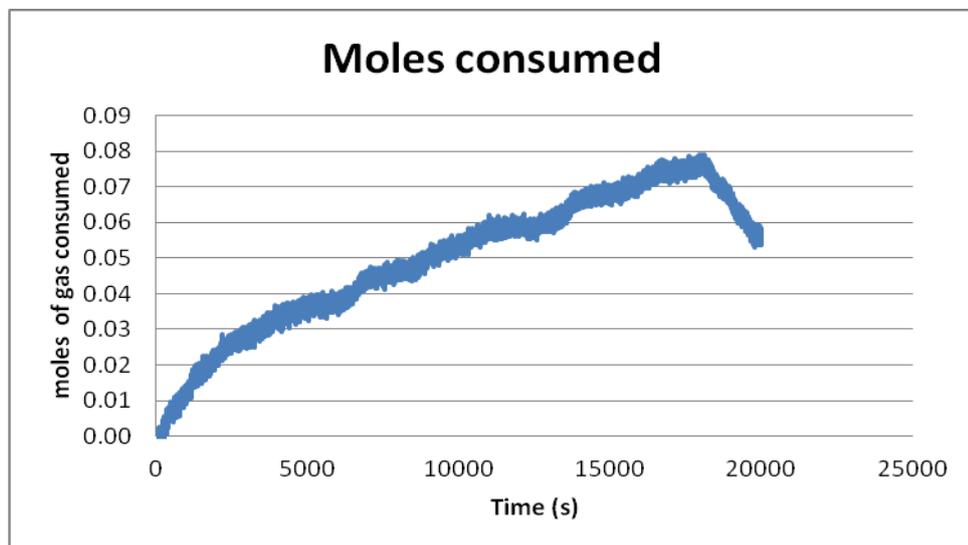


Figure 4.8: Moles Consumption for Experiment 2

Similar to experiment 1, the mole consumption for experiment 2 also increases with time. However the amount of maximum gas moles consumed is much lesser; around 0.08 moles/s.

Rate Constant

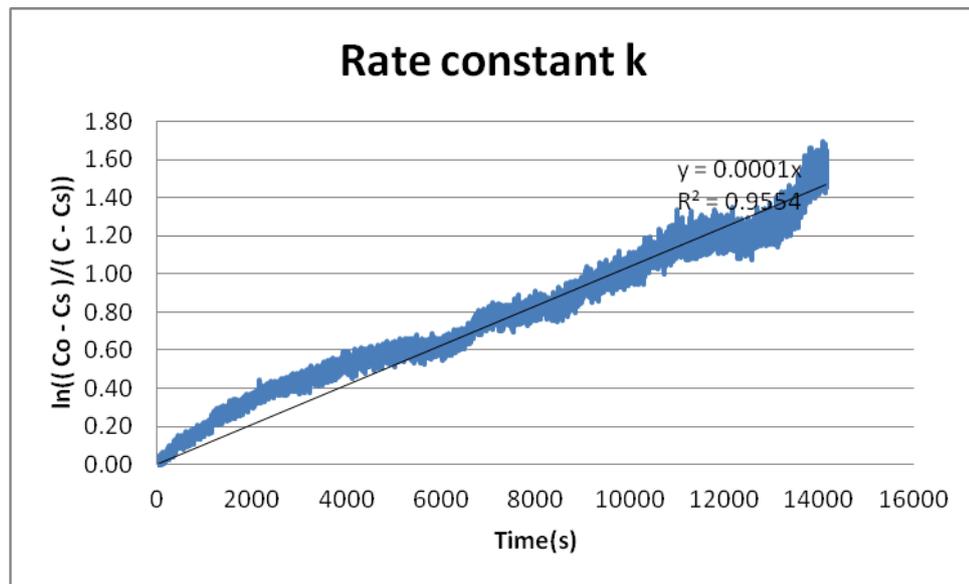


Figure 4.9: Rate constant for Experiment 2

As can be seen in figure 4.9, the rate constant for experiment 2 is smaller than that for experiment 1. The slope of the regression line gives the value of the rate constant. In this case the value $k = 0.0001$ per second.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This study reports the kinetics data of hydrate formation for two different composition mixtures of CH₄ & CO₂. By comparing the results, it is found that the gas mixture with the higher CO₂ content has a faster rate of hydrate formation and shorter induction time as compared to gas mixture with higher CH₄ content. This finding is in agreement with the study by Golombok et.al. (2009). According to them, within the same range degree of super saturation, the crystal growth of carbon dioxide hydrates is faster than that of methane hydrate.

Furthermore, results from GC analysis for both the experiments showed that the amount of CO₂ inside the hydrate was roughly four times higher than the amount of CH₄. This shows that CO₂ gas is always preferentially taken up by the hydrate irrespective of whether the gas mixture had higher or lower CO₂ content.

A reason for higher uptake of carbon dioxide within the hydrate could be because carbon dioxide hydrates are thermodynamically more stable than CH₄ hydrates. Another important factor is that CO₂ is much more soluble in water than CH₄ which greatly facilitates its mass transfer into the hydrate structure.

These results indicate that the separation of CO₂ by hydrate formation is not only favorable from a thermodynamic point of view but also from kinetics aspects.

Hence it is highly recommended to perform more experiments using different gas mixture compositions under similar conditions in order to further confirm the kinetic behaviour of mixed methane and carbon dioxide hydrates. Such data could be very useful in the designing of the prospective hydrate based technologies for carbon dioxide separation from natural gas.

REFERENCES

- [1] Sloan, E.D and Koh, C.A. 2008, *Clathrate Hydrates of Natural Gases*, 3rd ed., CRC Press
- [2] Sabil, K.M., Malik, N.A., Hazim, M.A and Behzad, P. *Effects of SDS Solution on Kinetic of Formation of Carbon Dioxide Hydrate*, IEEE Conference Publishing, Universiti Teknologi PETRONAS, Malaysia.
- [3] Sabil, K., M., *Phase Behavior, Thermodynamics and Kinetics of Clathrate Hydrates Systems of Carbon Dioxide in Presence Tetrahydrofuran and Electrolytes*. Master Thesis, Universiti Sains Malaysia, Malaysia, 2009
- [4] Linga, P., Kumar, R and Englezos, P. 2007, *Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures*, Chemical Engineering Science, 62(2007), pp. 164268–4276
- [5] Cláudio, P and Paulo, L.C. 2008, *Modelling of hydrate formation kinetics: State-of-the-art and future directions*, Chemical Engineering Science, 63(2008), pp. 2007–2034
- [6] Belandria, V., Mohammadi, A and Richon, D. 2010, *Phase equilibria of clathrate hydrates of methane + carbon dioxide: New experimental data and prediction*, Chemical Engineering Science, 296(2010), pp. 60-65
- [7] Unruh, C.H., Katz, D.L., *Trans. AIME*, **186**, 83 (1949)
- [8] Adisasmito, S., Frank, R.J., Sloan, E.D., *J. Chem. Eng. Data*, **36**, 68 (1991)
- [9] Ohgaki, K., Takano, K., Sangawa, H., Matsubara, T., Nakano, S., *J. Chem. Eng. Jpn.*, **29**, 478 (1996)
- [10] Fan, S. -S., Guo, T.-M., *J. Chem. Eng. Data*, **44**, 829 (1999)
- [11] Seo, Y.-T., Lee, H., Yoon, J.-H., *J. Chem. Eng. Data*, **46**, 381 (2001a)
- [12] Seo, Y.-T., Lee, H., *J. Chem. B.*, **105**, 10084 (2001b)
- [13] Hachikubo, A., Miyamoto, A., Hyakutake, K., Abe, K., Shoji, H., in *Proc. Fourth International Conference on Gas Hydrates* (Mori, Y.H., ed.), Yokohama, May 19-23, p.357 (2002)
- [14] Ohgaki, K., Makihara, Y., Takano, K. *J. Chem. Eng. Japan*, 1993, 26 (5), pg. 558-564

APPENDIX 1

MATLAB Formula for Z (compressibility factor calculation)

```
clear all
[data_hdr] = xlsread('P-T Values.xls',1);

P = data(1:length(data),1);
T = data (1:length(data),2);
a = data (1:length(data),3);
b = 0.000026671
R = 0.00000831

A = (a.*P)./(R*T).^2;
B = (b*P)./(R*T);

for i = 1:length(P)
i = 89
eqn = [1 -(1-B(i)) (A(i)-(3*B(i).^2)-(2*B(i))) -(A(i).*B(i)-(B(i).^2)-(B(i).^3)) ];
rt(:,i) = max(real(roots(eqn)))
end
```

APPENDIX 2

Sources of some available data in open literature on measurements of hydrate growth rates are as below:

- Ohgaki, K., Makihara, Y., Takano, K. *J. Chem. Eng. Japan*, 1993, 26 (5), pg.558-564
- Malegaonkar, M. B., Dholabhai, P.D., Bishnoi, P.R., *Canadian J. Chem. Eng.*, 1997, 75, pg. 1090-1099.
- McCallum, S. D., Riestenberg, D. E., Zatsepina, O. Y., Phelps, T. J., *J. Petroleum Sci. Eng.*, 2007, 56, pg. 54-64.
- Giavarini, C., Maccioni, F., Politi, M., Santarelli, M.L., *Energy & Fuels*, 2007, 21, pg. 3284-3291.

Sources of some available data in open literature on phase equilibria for binary-guest mixtures containing methane and carbon dioxide are as below:

- Unruh, C.H., Katz, D.L., *Trans. AIME*, **186**, 83 (1949)
- Adisasmito, S., Frank, R.J., Sloan, E.D., *J. Chem. Eng. Data*, **36**, 68 (1991)
- Fan, S. -S., Guo, T.-M., *J. Chem. Eng. Data*, **44**, 829 (1999)
- Seo, Y.-T., Lee, H., Yoon, J.-H., *J. Chem. Eng. Data*, **46**, 381 (2001a)
- Seo, Y.-T., Lee, H., *J. Chem. B.*, **105**, 10084 (2001b)
- Hachikubo, A., Miyamoto, A., Hyakutake, K., Abe, K., Shoji, H., in *Proc. Fourth International Conference on Gas Hydrates* (Mori, Y.H., ed.), Yokohama, May 19-23, p.357 (2002)