Estimation of Enthalpy of Dissociation and Hydration Number in Single Hydrate Systems

by

Nur Farhanah Nadhirah binti Mohammad Adam

(9428)

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

JULY 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Estimation of Enthalpy of Dissociation and Hydration Number in Single Hydrate Systems

by

Nur Farhanah Nadhirah binti Mohammad Adam

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

JULY 2010

Approved by,

(Dr. Khalik M. Sabil)

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

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 by unspecified sources or persons.

Nur Farhanah Nadhirah bt Mohammad Adam

ACKNOWLEDGEMENT

Praise to God, I managed to complete my final year research project in two semesters. A lot has transpired during this period of time and I am in debt to so many who had made this course an illuminating and enriching venture. I would like to thank the people involved in making this project a success.

Firstly, I am heartily thankful to my supervisor, Dr. Khalik for his enlightening supervision and countless hours spent in sharing his insightful understanding, profound knowledge and valuable experiences from the initial to the final level enabled me to develop an understanding of the project. I also would like to express my gratitude for his endless advice and support during my project period.

Not forgotten to my family for providing everything, such as money, to buy anything that are related to this project work and their support, which is the most needed for this project. They also supported me and encouraged me to complete this task so that I will not procrastinate in doing it.

I am grateful to have an endless supports from my friends who have been giving me courage and sharing their thoughts throughout this course in order to complete my final year project. Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the project.

ABSTRACT

This report is about the study on clathrate hydrates. Clathrate hydrates have been intensively studied due to its potential to be one of the energy sources. This project focuses on clathrate hydrates thermodynamics properties which are the enthalpy of dissociation and hydration number. Experimental work can be done to estimate both values, the enthalpy of dissociation and hydration number. However, due to time constraints as well as the limited laboratory equipments, the value will be determined by using theoretical calculation. By using the Clapeyron equation, both enthalpy of dissociation and hydration for selected systems will be estimated. The Clapeyron equation is chosen because it takes into account the volume changes of the systems and the solubility of water in gases at appropriate temperature and pressure. Available data such as phase equilibrium data are the key important in determining the values. The value estimated will be validated with the previous studied data. The values estimated will be documented and these values can be very useful as a base in order to investigate the potential of clathrate hydrates to be one of the energy sources.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Clathrate hydrates are clathrate compounds in which the host molecule is water and the guest molecule is typically a gas. Without the support of the trapped molecules, the lattice structure of clathrate hydrates would collapse into conventional ice crystal structure or liquid water. Most low molecular weight gases (including O_2, H_2, N_2, CO_2, CH_4, H_2S, Ar, Kr, and Xe) as well as some higher hydrocarbons will form hydrates at suitable temperatures and pressures.

In addition, clathrate hydrates are not chemical compounds as the sequestered molecules are never bonded to the lattice. The formation and decomposition of clathrate hydrates are first order phase transitions, not chemical reactions. Their detailed formation and decomposition mechanisms on a molecular level are still not well understood.

Clathrate hydrates are well known structures that were considered for many years as harmful by the oil and gas industry because of their annoying tendency to plug pipelines. (Chatti *et al.*, 2005) Intense research on natural gas hydrates was conducted by the oil and gas industry when it was pointed out that these compounds were responsible for plugging natural gas pipelines. (Hammerschmidt, 1934) In fact, light gases such as methane or ethane present in petroleum products are easily trapped as guest molecules in hydrate structures.

But somehow, clathrate hydrates are now attracting renewed interest in many fields. The reasons are that because of the hydrates widespread occurrences and the potential of the hydrates to be resource for energy production causes global climate changes and things related. Due to this, clathrate hydrates have successfully attracted the attention of the scientific community of worldwide to conduct a study about it.

Gas hydrates naturally found in deep seas and permafrost may provide a large amount of methane. Methane hydrates stored within and trapped below the hydrated sediments has a large energy potential. It is estimated to be twice the amount of total fossil fuel energy reserves of the world. Gas hydrates like methane hydrates is appear to be a candidate as an alternative energy that can act as a clean fuel, provided that the environmental impact is taken into consideration.

Even though clathrate hydrates can be considered as the main sources of energy for the future, gas hydrate deposits might represent a real threat to the environment. Indeed, when considering offshore hydrates as a global methane reservoir, exploitation of these sediments in unfavorable circumstances could drastically modify the marine ecosystem and even generate underwater gas blowouts. (Glasby, 2003) Moreover, destabilizing hydrate sediments plays an undeniable role in climate change.

Other positive applications include carbon dioxide sequestration (Lee *et al.*, 2003), separation and natural gas storage (Sloan, 2000) and transportation. It is all due to the high gas concentration of the clathrate hydrates. Finally, the use of their dissociation energy can be applied in refrigeration applications, such as cool storage or air conditioning. (Tanasawa *et al.*, 2002; Fournaison *et al.*, 2004)

For the industry, in order to utilize clathrate hydrates' energy potential in any applications, one needs a deep understanding and knowledge about clathrate hydrates compound especially in terms of its thermodynamics properties. These thermodynamics properties such as its phase equilibrium data are highly crucial in order to develop clathrate hydrates potential to be used in the industry. Study on thermodynamics properties of clathrate hydrates can be done via experimental procedure such as differential scanning calorimetric.

Previous research work done by the scientists and researchers can be used as a basis to understand the clathrate hydrates behavior. The temperature and pressure data as well as the phase's condition data has been collected by them. These data can be used to develop the phase equilibrium diagram. From the phase equilibrium diagram, the behavior of clathrate hydrates can be known and help to estimate which region of temperature and pressure that has high energy level.

Moreover, any applications developed can suits the clathrate hydrates behavior. Once successful, the potential of clathrate hydrates to be one of the energy sources can be known and commercialized publically.

1.2 PROBLEM STATEMENT

Theoretically, the enthalpy of dissociation and hydration number of clathrate hydrates can be estimated by using the analysis of the Clapeyron equation. Based on previous work done by Anderson (2003, 2004), he clearly stated that, this analysis takes into account the finite volumes of the condensed phases, the non-ideality of the vapor phase, and the solubility of gases in water.

Anderson (2003, 2004) analysis is an improvement on previous analyses because it uses the Clapeyron equation directly which avoided the simplifying assumptions that must be made to use the Clausius-Clapeyron equation. In his work, he utilizes recently published data (Anderson, 2002) for the solubility of gases in water in the appropriate temperature and pressure region.

Based on Anderson studies, it is my attempt to conduct an analysis to estimate the enthalpy of dissociation and hydration number for selected clathrate hydrates systems. If the comparison of his work with my research project are accurate, and obeys all the assumptions, then his method of analysis, the enthalpy of dissociation and hydration number can be used for other type of clathrate hydrates in the future.

As a preliminary step, the phase equilibrium data of single clathrate hydrates systems will be selected and studied. Other relevant data will be collected to be used in the calculation steps. The hydration number and enthalpy of dissociation of the single clathrate systems will be predicted by using the Clapeyron equation. From this, the results of calculation will be compared and validated.

From this work, it is expected that the Clapeyron equation can be use to predict the estimation of the hydration number and enthalpy of dissociation of selected single clathrate hydrates systems.

1.3 OBJECTIVES OF PROJECT, SCOPE OF STUDY AND OUTLINE OF REPORT:

By taking into account all the limitations for this research project, the objectives of this research are:

1. To estimate the enthalpy of dissociation and hydration number from the phase equilibrium data in a single clathrate hydrate systems.
2. To test the accuracy of the predicted result from the Clapeyron equation by using AAD% (average absolute deviation).
3. To compare the predicted result from the Clapeyron equation with the Clausius-Clapeyron equation.
4. To validate the estimated values with experimental result done by previous researchers.

The enthalpy of dissociation and hydration number can be determined by analysis of experimental work by using high pressure differential scanning calorimetry. However, due to the time constraints as well as the limited laboratory equipments, these both values are being estimated by using theoretical calculation in this project.

The scope of this project is to estimate the enthalpy of dissociation and hydration number of clathrate hydrate systems by doing analysis on the Clapeyron equation. Based on the equation there are certain values that need to be extracted from the series of mathematical calculation steps based on the phase equilibrium diagram. The estimated value for phase behavior collected will be used in the Clapeyron equation in order the get the estimated value for both the enthalpy of dissociation and hydration number.

In Chapter 2, the literature work is done to have a complete understanding about the aims of this research project. A strong knowledge about the structure of clathrate hydrates as well as the enthalpy of dissociation and hydration number can help to build a strong understanding to achieve the objectives of this research project.

The experimental data of several clathrate hydrates systems will be selected and studied. The experimental data involving the temperature and pressure has been collected by Sloan and Koh (2003). These data are highly crucial because it acts as a basis in order to develop the phase diagrams for the selected clathrate systems.

The analysis of data will only take into account in determining the enthalpy of dissociation and hydration number for the dissociation of solid hydrate to gaseous carbon dioxide and liquid water, and dissociation of solid hydrate to gaseous carbon dioxide and ice.

Since there are various types of clathrate hydrates, for this particular research project, only methane (CH_4) hydrate, carbon dioxide (CO_2) hydrate and ethane (C_2H_6) hydrate are chosen to be studied. For this research project, the temperature and pressure range selected from experimental data will be different for each type of hydrates systems.

In Chapter 3, the methodology or series of calculation steps involved are described. By referring to the calculation techniques done by Anderson (2003, 2004) and altering certain measures, all assumption that is used in the Clapeyron equation are taken into account. This is to ensure that the estimated result of enthalpy of dissociation and hydration number obtained will yield an accurate result.

The results of the estimated calculation for enthalpy of dissociation and hydration number of the methane hydrate and carbon dioxide are presented and discussed in Chapter 4. Here, the estimated value is also being validated with the previous work done by Anderson for methane hydrate and carbon dioxide hydrate. Finally, conclusions of the present work together with the future recommendations are presented in the Chapter 5.

CHAPTER 2: LITERATURE REVIEW

2.1 CLATHRATE HYDRATES

Clathrate hydrates were first discovered in 1810 by Sir Humphry Davy. In the early days, clathrate hydrates were only considered as a laboratory curiosity. In the 1930s clathrate formation turned out to be a major problem, clogging pipelines during transportation of gas under cold conditions. (Thomas, 2004) That time marked the beginning of an intense research effort on natural gas hydrates by the industry, the government, and the academia. Since then, study on hydrates has been intensified especially after discovery of the vast quantities of hydrates in the earth's crust. (Buffett and Archer, 2004)

Clathrate hydrates are a mixture of water and low molecular gases that crystallizes to form a solid 'ice plug' under appropriate conditions of temperature and pressure. They are formed when hydrogen-bonded water molecules form cage-like structures, known as cavities in the crystalline lattice. These cavities have to be at least partially filled with hydrate-forming molecules, also known as the 'guest molecules', in order to stabilize the structure. (Sabil, 2009)

Currently, clathrate hydrates have three structures that have been well studied which are structure I (sI), structure II (sII), and structure H (sH). These structures can be easily distinguished depending on the type and size of the guest molecule presents in the structure. Figure 2.1 shown below is the types of cavities present in each structure.

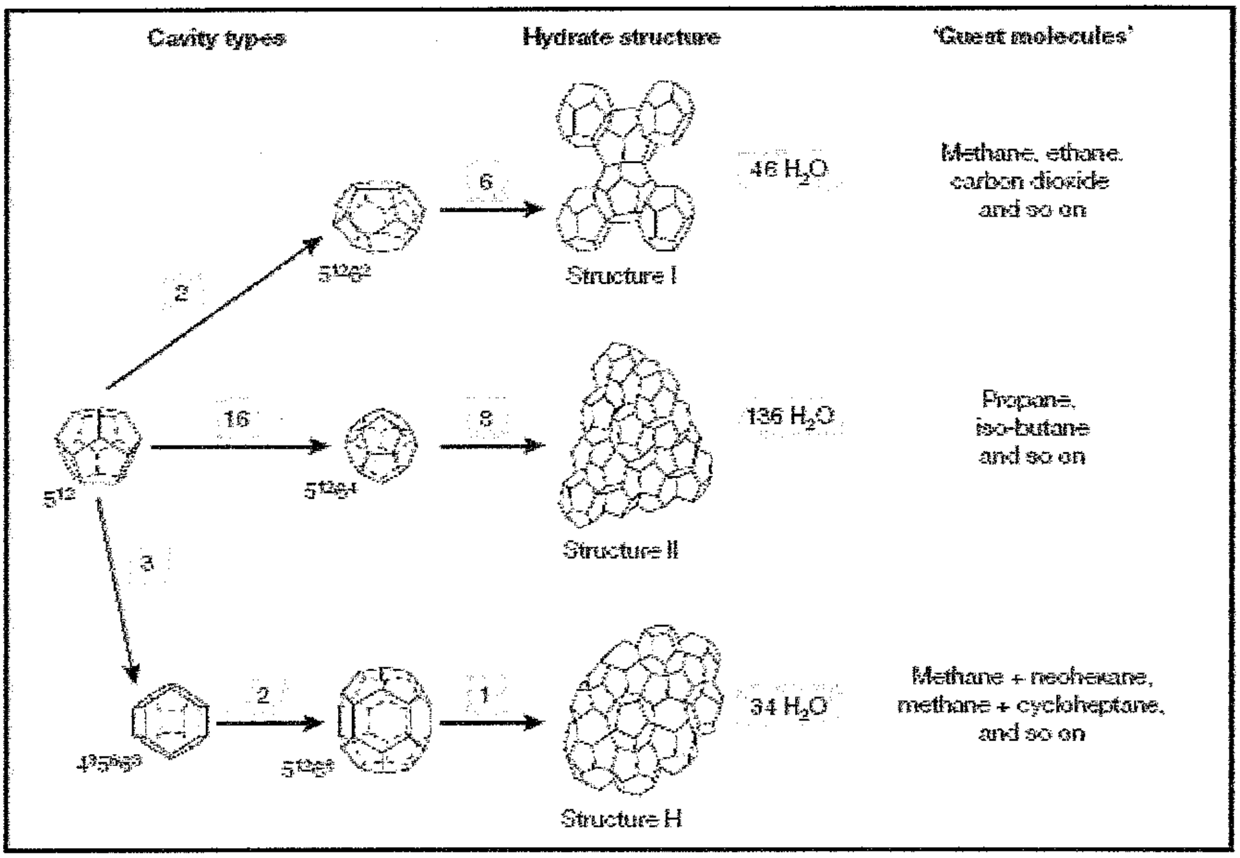

Figure 2.1: The three common hydrate unit crystal structures based on Sloan (2003).

The unit cell of structure I hydrate composts of two 5^{12} cages, six $5^{12}6^2$ cages and 46 water molecules. The unit cell of structure II hydrates composts of sixteen 5^{12} cages, eight $5^{12}6^4$ cages and 136 water molecules. Plus, structure H composts of three 5^{12} cages, two $4^35^36^3$ cages, one $5^{12}6^8$ cages and 34 water molecules. In all three structures, typically there is only guest molecule within each cage and in order to form hydrates, the size of the guest molecules cannot be too large or too small compared to the size of the cavities.

Inside each cavity resides a maximum of one of small guest molecules, typified by the eight guests associated with 46 water molecules in structure I ($2[5^{12}].6[5^{12}6^2].46H_2O$), indicating two guests in the 5^{12} and six guests in the $5^{12}6^2$ cavities of structure I. similar formulas applied for structure II and structure H are ($16[5^{12}].8[5^{12}6^4].13H_2O$) and ($3[5^{12}].2[4^25^66^3].1[5^{12}6^8].34H_2O$), respectively. (Sloan, 2000)

Based on Sloan (2000), structure I, a body-centered cubic structure forms with natural gases containing molecules smaller than propane. Consequently, structure I hydrates are found in situ in deep oceans with biogenic gases containing mostly methane, carbon dioxide and hydrogen sulfide. Structure II, a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane. Structure II represents hydrates from most natural-gas systems. Finally, structure H hydrates must have a small occupant (like CH_4, N_2, or CO_2) for the 5^{12} and $4^3 5^6 6^3$ cages. But, the molecules in the $5^{12}6^8$ cage can be as large like ethyl cyclohexane. Structure H has not been found commonly in natural-gas systems to date.

2.2 CLATHRATE HYDRATES PHASE BEHAVIOR

Based on the definition of hydrates, the amount of gas that dissolves in water to occupy between water molecules depends on the temperature and pressure. When the pressure is high, gas compresses and fills the spaces until they are saturated. Each component of gases such as methane and carbon dioxide has different water solubility. As a result, clathrate hydrates will form at different temperatures and pressures for different compounds. Figure 2.2 presents a typical phase diagram for a mixture of water with a light, pure hydrocarbon (HC), similar to that presented by McCain (1990). (Adewumi, 2008)

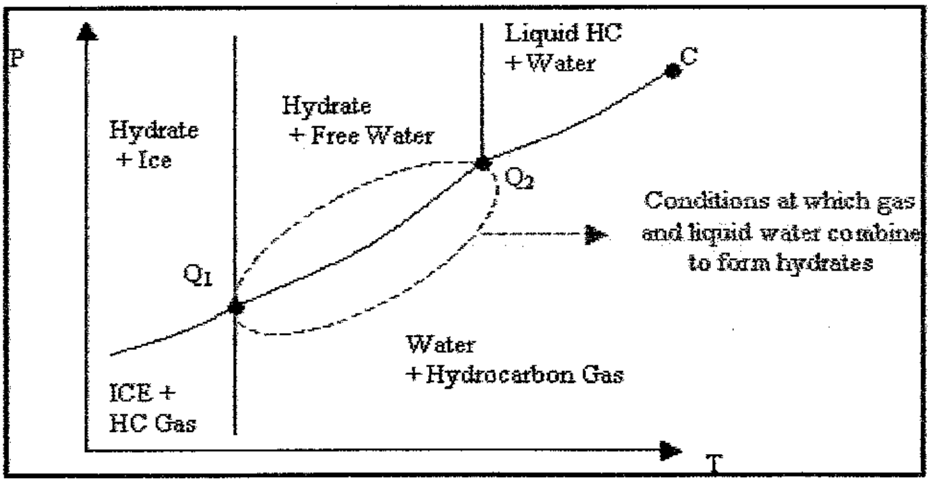

Figure 2.2: Phase Diagram for a Water/Hydrocarbon (HC) System. (Adewumi, 2008)

Based on the diagram, the behavior of the clathrate hydrates can be simplified into:

- The *three-phase critical point*, point C – the condition where the liquid and gas hydrocarbon merge into a single hydrocarbon phase in equilibrium with liquid water.

- The *upper quadruple point*, Point Q_2 – four phases which are liquid water, liquid hydrocarbon, gaseous hydrocarbon, and solid hydrate are found in equilibrium.

- The *lower quadruple point*, Point Q_1 – where typically occurs at 0 °C (ice freezing point) where four phases which are ice, hydrate, liquid water, and hydrocarbon gas are found in equilibrium.

The most important equilibrium line is the Q_1Q_2 segment. It represents the conditions for hydrate formation or dissociation. Phase Behavior thermodynamics is usually invoked for the prediction of the Q_1Q_2 hydrate formation/dissociation line. It also known as the equilibrium line where hydrates exist in the form of liquid/ice water + hydrates + vapor (natural gas).

When focus on this zone, the phase behavior of water/ hydrocarbon system is simplified to the schematic shown in Figure 2.3.

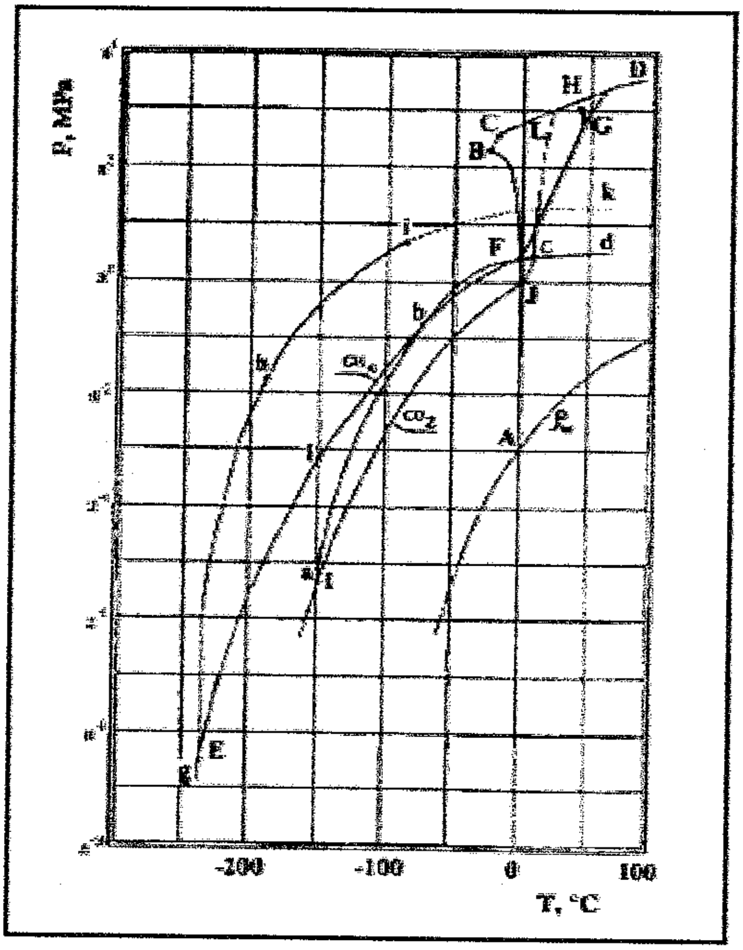

Figure 2.3: Conditions of methane hydrates and carbon dioxide hydrates formation.(Makogon, 1997)

Based on the diagram, it can be further simplified into:

- **ABCD** is the water – ice phase transition curve
- **ghik** is the methane vapor pressure curve
- **abcd** is the carbon dioxide vapor pressure curve
- **glbFGH** is the methane hydrate P – T equilibrium curve
- **aJcL** is the carbon dioxide hydrate P –T equilibrium curve
- **pw** is the water vapor pressure curve.

Plot above shows of pressure – temperature dependence of methane and carbon dioxide stability for low temperature and for high pressure respectively. It is very critical to have a deep understanding with the phase diagram as this diagram represents as the base for this project where data needed in the calculation will be extracted from the diagram. But first, the temperature and pressure data from previous experimental work will be taken from available sources.

2.2.1 Methane Hydrates

Methane hydrate will be the first hydrates to be studied in this project. Studies had shown that methane hydrate is among the hydrates that have the potential to be one of the energy sources. Methane forms a structure I hydrate. The phase behavior of methane hydrate can be seen clearly in the P-T diagram below. As shown, methane hydrate equilibrium diagram fulfill the similarity with the typical hydrates compound phase behavior. While it is stable at a temperature of up to around 273 K, at higher pressures methane hydrate remain stable up to 291 K.

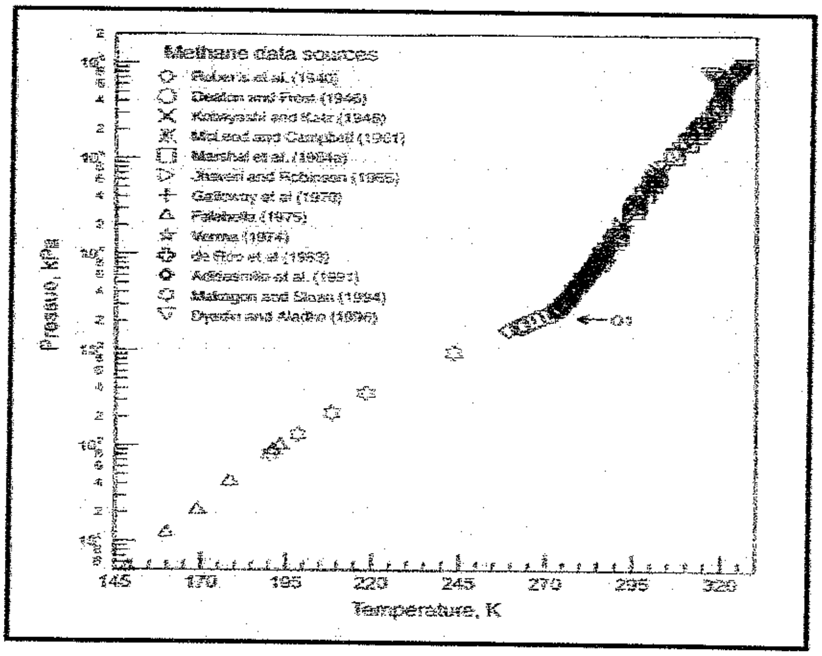

Figure 2.4: Three – Phases data for methane hydrate. (Sloan and Koh, 2003)

2.2.2 Carbon Dioxide Hydrates

Carbon dioxide forms structure I hydrate under appropriate pressure and temperature conditions. (Sabil, 2009) The phase behavior of carbon dioxide hydrate can be seen clearly in the P-T diagram below. (Sloan and Koh, 2003) As shown, carbon dioxide hydrate equilibrium diagram fulfill the similarity with the typical hydrates compound phase behavior. At any specified temperature, carbon dioxide hydrate will be stable as long as the pressure of the system is higher or equal to the equilibrium temperature of the system. The critical temperature is 284 K (11°C), where beyond that temperature; the carbon dioxide hydrate compound will reach the region of instability. No hydrates compound between carbon dioxide and water will be formed beyond this temperature.

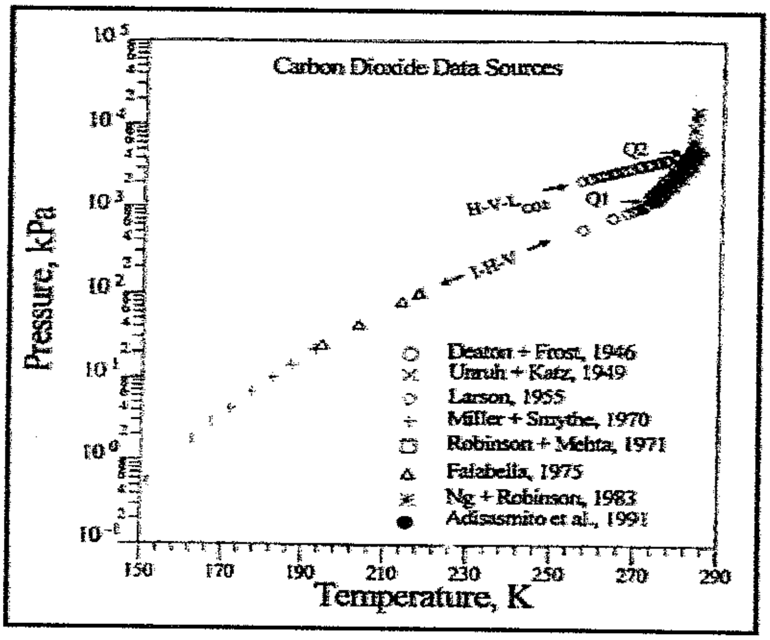

Figure 2.5: Three – Phases data for carbon dioxide hydrate. (Sloan and Koh, 2003)

2.2.3 Ethane Hydrates

Ethane hydrate will be the other hydrates to be studied in this project. Ethane forms a structure I hydrate. The phase behavior of ethane hydrate can be seen clearly in the P-T diagram below. Based on previous study, ethane hydrate data can be found experimentally. As shown, ethane hydrate equilibrium diagram fulfill the similarity with the typical hydrates compound phase behavior.

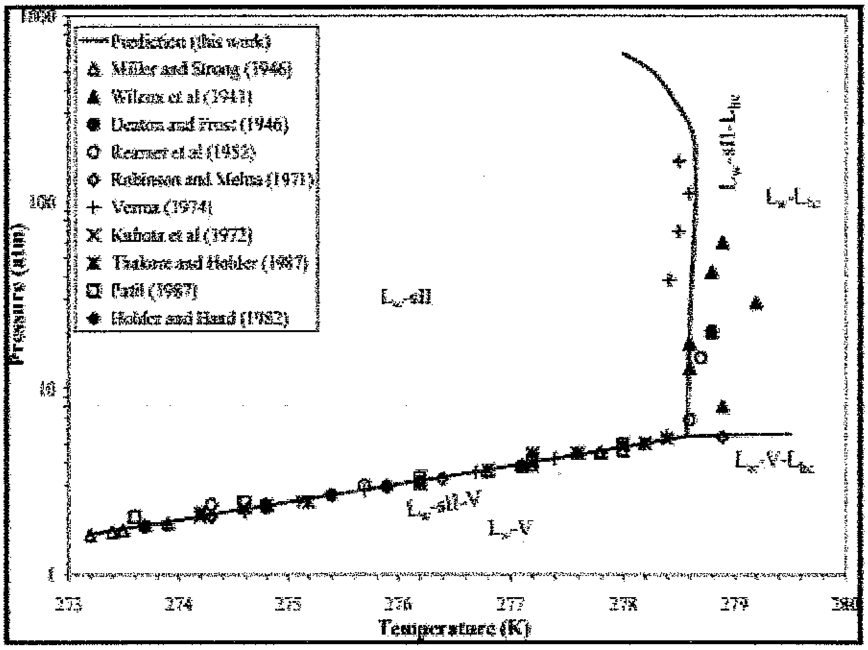

Figure 2.6: Three – Phases data for ethane hydrate. (Sloan and Koh, 2003)

2.3 ENTHALPY OF DISSOCIATION

Enthalpy of dissociation of hydrates is an endothermic process in which heat must be supplied externally to break the hydrogen bonds between water molecules and the Van der Waals interaction forces between the guest molecules of the hydrate lattice to decompose the hydrate to water and gas. (Sloan, 2003) The different methods can be used in order to measure the enthalpy of dissociation, ΔH whether it is done theoretically or experimentally. Theoretically, the approximation value of ΔH can be estimated using the Clapeyron equation or the Clausius – Clapeyron equation.

In the most thermodynamic case, the Clapeyron equation is used with pure components to obtain the heat of dissociation from pure component phase's data. The Clapeyron equation is one the primary successes of thermodynamics, because it enables the calculation of ΔH, which is difficult to measure, from easily available properties of temperature and pressure. The analysis using the Clapeyron equation must take into account, the non-ideality of the gas phase, the finite volume of the condensed phases and the solubility of the gas in liquid water.

As Van der Waals and Platteeuw (1959) point out, however, the application of the Clapeyron equation is thermodynamically correct, as long as the system is uni-variant and relates the enthalpy changes of a phase-equilibrium reaction to the volumetric properties of the reactants and products along the phase boundary.

The Clapeyron equation relates the differential pressure change in dp that accompanies a differential pressure change dT in a system where two or more phases are in equilibrium. The equation is presented without derivation as,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \qquad (1)$$

It was suggested also by van der Waals and Platteeuw (1959) that the Clapeyron equation could be applied to calculate the heat of decomposition of the single guest clathrate hydrate systems along the three-phase equilibrium line.

According to Gibbs phase rule, the single guest clathrate hydrates system for example; methane hydrate is uni-variant at the three-phase equilibrium conditions.

Gibbs phase rule: $F = C - P + 2$,

And $C = 2$, $P = 3$

Hence, $F = 1$.

Where F is the degree of freedom, C = number of components, P = number of phases.

The heat of dissociation can be calculated from the slope of the three-phase line and the change in volume, ΔV using the Clapeyron equation for example, methane hydrate to water and gas reaction in shown below,

$$\frac{dp}{dT} = \frac{\Delta H^{H \to W+G}}{T \Delta V^{H \to W+G}} \Rightarrow \Delta H^{H \to W+G} = T \Delta V^{H \to W+G} \frac{dp}{dT} \tag{2}$$

Where $\Delta V = V_G + V_W - V_H$

Recently Anderson, (2003, 2004) calculated the heat of dissociation of pure methane and carbon dioxide hydrates using the Clapeyron equation. The analysis accounts for the change in the exact volume of hydrate, gas, and water/ ice phases. The slope of the three-phase equilibrium curve at certain temperature was determined by first developing a pressure vs. temperature diagram based on the available data from Sloan Jr. (2003).

From the graph, the dp/ dT can be determined. The calculation for ΔV will be determined according to the volume for each region.

- V_G refers to the molar volume of pure methane vapor at certain temperature and pressure.

- V_W is referring to the sum of molar volume for both; liquid water and methane.
- V_H refers to the molar volume of hydrates which comes from the experimental value done by previous researcher.

According to Anderson (2004), the term ΔV is the part of the Clapeyron equation that presents the most difficulty. As the temperature increases over the stability field of the hydrate, dp/dT becomes very large and ΔV becomes correspondingly very small. It is necessary to find accurate representations of the volumes of each of the phases in equilibrium, and to account for how these vary with the temperature and pressure.

Later on, ΔH value can be estimated by adding up all this value. The important step above is needed, in order to calculate the enthalpy of dissociation of both methane hydrate and carbon dioxide hydrate. Mathematical tools involving differentiation as well as the integration can be very useful in order to simplify the Clapeyron equation.

2.4 HYDRATION NUMBER

Calculation for hydration number can only be done only after the calculation for the enthalpy of dissociation is completed. De Forcrand had proposed his method by using the Clapeyron equation to obtain the heat of dissociation from phase diagram, pressure-temperature data, then considers the equilibrium of gas and η mol of liquid water (or ice) with hydrates on either side of the ice point. For example:

$$\text{Hydrates} \rightarrow \text{Gas} + n(\text{liquid water}) \quad \Delta H_1 \tag{3}$$

$$\text{Hydrates} \rightarrow \text{Gas} + n\,(\text{ice}) \quad \Delta H_2 \tag{4}$$

$$n\,(\text{liquid water}) \rightarrow n\,(\text{ice}) \quad \Delta H_3 \tag{5}$$

$$\Delta H_3 = \Delta H_1 - \Delta H_2 \tag{6}$$

Enthalpy of fusion (ΔH_f) of water/ ice is well known, n can be obtained by dividing the difference in ΔH values (ΔH_1 - ΔH_2) with the heat of fusion of water/ ice (ΔH_f). n is equal to moles of water (ice) converted to hydrates.

The theoretical considerations and observations reported in the literature on cage occupancy of the hydrate structures can be used to justify the calculated hydration number. The hydration number is calculated based on the number of cavities occupied by gaseous molecules in the hydrate cage. (Khalik, 2009)

CHAPTER 3: METHODOLOGY

3.1 EVALUATION OF CLATHRATE HYDRATES PHASE BEHAVIOR

Before any calculation steps can be done, understanding the hydrates component is highly important. A strong literature review need to be done based on the previous study in order to understand the problem and find the best solution to get the accurate result. Among the segments that must be fully understand are phase behavior including the phase diagram and formation condition of both methane hydrate and carbon dioxide hydrate.

From here, the value of the d*p*/d*T* expression in the Clapeyron equation will be extracted from the phase diagram. This value need to be extracted carefully to ensure that the value is taken at the correct temperature and pressure as well as the phases of the hydrates. These data are highly important in order to complete the next step to determine the enthalpy of dissociation.

Based on Anderson (2004), he has come out with the steps of solving in order to get the estimated value of enthalpy of dissociation and hydration number. These series of steps will be used as the method to validate the estimated value of enthalpy of dissociation and hydration number for single systems which are methane hydrate, carbon dioxide hydrate and ethane hydrate.

Anderson (2004) has highlighted the steps involved for methane hydrate and carbon dioxide hydrate respectively:

3.1.1 Methane Hydrate

The enthalpy of dissociation of methane hydrate will be determined from the two equations represent the dissociation of:

- Methane hydrate to liquid water & gaseous methane

$$CH_4.nH_2O_{(s)} \rightarrow CH_4{}_{(g)} + nH_2O_{(l)} \qquad (\Delta H_l) \qquad (7)$$

- Methane hydrates to ice water & gaseous methane.

$$CH_4.nH_2O_{(s)} \rightarrow CH_{4\,(g)} + nH_2O_{(s)} \qquad (\Delta H_2) \qquad (8)$$

Determination of ΔH_1 and ΔH_2 will be done from an analysis of the pressure and temperature (p, T) behavior along the liquid, hydrate, vapor (L, H, V) and ice, hydrate, vapor (I, H, V) equilibrium lines respectively.

According to Anderson (2004), there is a small complication with regard to reaction for ΔH_1, the liquid in equilibrium with hydrate is not pure water, and rather it is water that is saturated with respect to methane at the appropriate temperature and pressure.

The mole fraction of methane in the water in equilibrium with the hydrate is x_{CH_4}. Then n moles of water supplies nx_{CH_4} / (1 - x_{CH_4}) moles of methane to the hydrate; while the rest is comes from the gas. Thus, reaction for ΔH_1 must be analyzed as the sum of two terms:

$$CH_4.nH_2O_{(s)} \rightarrow \left(1 - \frac{nxCH_4}{1-xCH_4}\right)CH_{4\,(g)} + nH_2O_{(l,\ CH4\ sat)} \qquad (\Delta H_{1a}) \qquad (9)$$

$$CH_4.nH_2O_{(s)} \rightarrow \left(\frac{nxCH_4}{1-xCH_4}\right)CH_{4\,(g)} + nH_2O_{(l)} \qquad (\Delta H_{1b}) \qquad (10)$$

The term H_2O (l, CH_4 sat) refers to a mole of liquid water which is saturated with respect to methane at the given temperature and pressure. The Clapeyron equation will be used to find ΔH_{1a}, while solubility data will be used to find ΔH_{1b}. For ΔH_2, enthalpy can be determined directly because solubility of methane in ice is negligible.

The Clapeyron equation is presented without derivation gives;

$$\Delta H = T\,\Delta V\,\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) \tag{11}$$

From there, the analysis begins with the determination of ΔH_2 because it is straightforward and the value of ΔH_2 will be used in order to find ΔH_1 and n.

The $(p,\ T)$ of three phase equilibrium (ice, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Roberts *et al.* (1940)
- Falabella (1975)
- Deaton and Frost (1946)
- Makogon and Sloan (1994)

The $(p,\ T)$ data will be plotted as ln $(p/$ MPa) vs. $K/$T graph. Then, the graph will be least-squares fitted to a third order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_2 will be calculated manually while; the d$p/$ dT will be calculated using the equilibrium graph plotted before. Based on the graph, the d$p/$ dT can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i\left(\frac{K}{T}\right)^i \tag{12}$$

The function is differentiated with respect to $1/T$ that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i\left(\frac{K}{T}\right)^i \tag{13}$$

Finally, dp/ dT at each temperature and pressure are found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2}\frac{\mathrm{d}\ln(p)}{\mathrm{d}\left(\frac{1}{T}\right)} \tag{14}$$

The fit parameters of a_0, a_1 and a_2 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_2. ΔV_2 is equal to;

$n\ V_{ice}$ (volume of n moles ice) + V_{CH_4} (volume of 1 mole methane vapor) – V_{hyd} (volume of hydrate containing 1 mole methane).

(15)

The parameters for each sections of volume can be obtained from the data collected by previous studies and NIST webbook. From there, the Clapeyron equation for ΔH_2 can be easily calculated once the value for ΔV_2 and dp/ dT has been determined for selected temperature and pressure.

The next step is to determine the ΔH_1, we starts with ΔH_{1a}.

The (p, T) of three phase equilibrium (liquid, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Roberts *et al.* (1940)
- Marshall *et al.* (1964a)
- Jhaveri and Robinson (1965)
- Galloway *et al.* (1970)
- Deaton and Frost (1946)
- Kobayashi and Katz (1949)
- McLeod and Campbell (1961)
- Verma (1974)

- de Roo *et al.* (1983)
- Thakore and Holder (1987)
- Adisasmito *et al.* (1991)
- Makogon and Sloan (1994)

The (p, T) data will be plotted as ln (p/ MPa) vs. K/T graph. Then, the graph will be least-squares fitted to a sixth order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_{1a} will be calculated manually while; the dp/ dT will be calculated using the equilibrium graph plotted before. Based on the graph, the dp/ dT can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i (\frac{K}{T})^i \tag{16}$$

The function is differentiated with respect to 1/ T that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i (\frac{K}{T})^i \tag{17}$$

Finally, dp/ dT at each temperature and pressure are found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2} \frac{\mathrm{d}\ln(p)}{\mathrm{d}\,(\frac{1}{T})} \tag{18}$$

The fit parameters of b_0, b_1, b_2, b_3, b_4 and b_5 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_{1a}. ΔV_{1a} is equal to;

$\left(1 - \frac{nxCH_4}{1-xCH_4}\right)$ V_{CH4} (volume of n moles ice) + nV_{liq} (volume of 1 mole methane vapor) – V_{hyd} (volume of hydrate containing 1 mole methane.

(19)

The parameters for each sections of volume can be obtained from the data collected by previous studies. Each of the sections will be determined according to the function. From there, the Clapeyron equation for ΔH_{Ia} can be easily calculated once the value for ΔV_{Ia} and $dp/\ dT$ has been determined for selected temperature and pressure.

ΔH_{Ib} can determined from the solubility data. The solubility can be evaluated by the available data using the Krichevsky-Kasarnorvsky (1935) equation;

$$\ln\left(\frac{f}{x_{CH4}}\right) = \ln K_H + \frac{V\infty_{CH4,H2O}\,(p - p^s)}{RT}$$

(20)

Where f, fugacity of CH_4 in the gas phase; x_{CH4}, mole fraction of CH_4 dissolved in the liquid phase; K_H, Henry's law constant; $V\infty_{CH4,H2O}$, partial molar volume of CH_4 in water at infinite dilution; p, total system pressure; p^s, vapor pressure of water at temperature T.

The partial molar volume, $V\infty_{CH4,H2O}$ at infinite dilution is independent of pressure and slightly dependent of temperature and can be determined by;

$$ln\ \left[V\infty_{CH4,H2O}\ /(\mathrm{m}^3.\mathrm{mol}^{-1}\right] = -10.275 + 1.23 \times 10^{-3}\left(\frac{\mathrm{T}}{K} - 273.15\right)$$

(21)

The methane solubility is found from the measured value from Servio and Englezos (2002). Because of the mole fraction x_{CH4} is so low, the enthalpy of solution per mole of methane can be equated with little error to the partial molar enthalpy of solution at infinite dilution which denoted by$\Delta H\infty_{CH4,H2O}$.

Based on Benson and Krause (1989), $\Delta H\infty_{CH4,H2O}$ can be known by equation;

$$\Delta H\infty_{CH4,H2O} = R\frac{d\ln K_H}{d(\frac{1}{T})} - T\frac{dV\infty_{CH4,H2O}}{dT}(p - p^s) + V\infty_{CH4,H2O}(p - p^s) + TV\infty_{CH4,H2O}(\frac{dp^s}{dT})$$

(22)

The second term in equation is negligible since $V\infty_{CH4,H2O}$ is almost independent of T. also, the fourth term is negligible due to the smallness of the water vapor pressure at the temperatures of hydrate formation. Once calculated, the $\Delta H1_b$ can be determined just by simply multiply the expression of $\Delta H\infty_{CH4,H2O}$ with the$\left(-\frac{nxCH_4}{1-xCH_4}\right)$.

Finally, the enthalpy of dissociation of methane hydrate ΔH_l can be known by, the total submission of $\Delta H_{la} + \Delta H_{lb}$. For the calculation of hydration number can only be done once the enthalpy of both reactions has been determined.

The difference between enthalpy of both reactions will be divided with the enthalpy of fusion of water and the hydration number can be known.

3.1.2 Carbon Dioxide Hydrate and Ethane Hydrate

Basically, the steps to calculate the enthalpy of dissociation for carbon dioxide hydrate and ethane hydrate are the same with the calculation steps for methane hydrate. The steps can be referred from Anderson (2003). However, there are some parameters for carbon dioxide hydrate that will be not the same as methane hydrate and these parameters must be carefully selected to ensure the value estimated is accurate.

The steps in determining the enthalpy of dissociation for carbon dioxide hydrate and ethane is discussed in the Appendix I. If the both method is proven correctly, it will be used as a basis in solving the estimated value of enthalpy of dissociation and hydration number for other clathrate hydrates single systems such as ethane hydrate given that the parameters will be suited according to the type of hydrates.

3.2 VALIDATION

As mentioned earlier, using the Clapeyron equation, the enthalpy of dissociation as well as the hydration number can be estimated. Once value has been estimated, the important keys that need to be considered in this part are:

- To test the accuracy of the predicted result from the Clapeyron equation for clathrate hydrates selected systems.
- To compare the predicted result from the Clapeyron equation with the Clausius-Clapeyron equation.
- To validate the estimated values with experimental result for clathrate hydrates selected systems.

Previous studied result is important as it acts as the basis of the calculation work. The previous studied will be fully studied and some modifications on calculation that need to be done will be taken to get more accurate result. For this project, the previous studied result by Anderson (2003, 2004) will be fully utilized in order to get the estimated value for enthalpy of dissociation for methane hydrate and carbon dioxide hydrate.

Moreover, the estimated value from the calculation will be validated with the previous studied data done by Anderson (2003, 2004) and other experimental result done by previous researchers. Once comparison is made, the error should be at low value, the estimated value from the calculation must be low value or equally same as experimental value done by previous studied result.

3.3 TOOLS AND SOFTWARE REQUIRED

For this project, all the equilibrium data will be collected by using the Microsoft Excel. As mention in the steps above, the graph of pressure versus temperature will be plotted accordingly for methane hydrate and carbon dioxide hydrate. The slope of the graph will be determined to fit the parameters inside the Clapeyron equation. This software is very suitable to use as it will help in ensuring the diagram is correct and value determined by the software is essential to be used in the Clapeyron equation.

For manual calculation, mathematical tools especially from engineering mathematics subjects are very essential to use. The statistical analyses tools will be used to ensure that the value estimated from the calculation are accurate and the error must be at low value. For instance, AAD% (average absolute deviation) test will be used to determine the accuracy for both estimated value calculated and previous studied result.

3.4 GANTT CHART

No	Project Activities	Week																		
		1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	16	17	18
1	Calculation and Validation Works								BREAK											
2	Consultation with Supervisor																			
3	Submission of Progress Report 1				▨															
4	Submission of Progress Report 2														▨					
5	Poster Exhibition (Pre-EDX)													▨						
6	Submission of Dissertation (Softbound)																▨			
7	Oral Presentation																			▨
8	Submission of Dissertation (Hardbound)																			▨

Completed

Compulsory ▨

CHAPTER 4: RESULT AND DISCUSSION

Based on the Anderson (2003, 2004) method of calculating the enthalpy of dissociation and hydration number is followed, the result for three different clathrate hydrates is calculated respectively;

4.1 METHANE HYDRATE

4.1.1 Enthalpy of Dissociation of Clathrate Hydrate to Methane Vapor and Ice (ΔH_2)

The equation that represents the dissociation of methane hydrates to ice water & gaseous methane.

$CH_4.nH_2O_{(s)} \rightarrow CH_{4\,(g)} + nH_2O_{(s)}$ (ΔH_2) (8)

The graph of (p,T) data plotted for ΔH_2 is shown below:

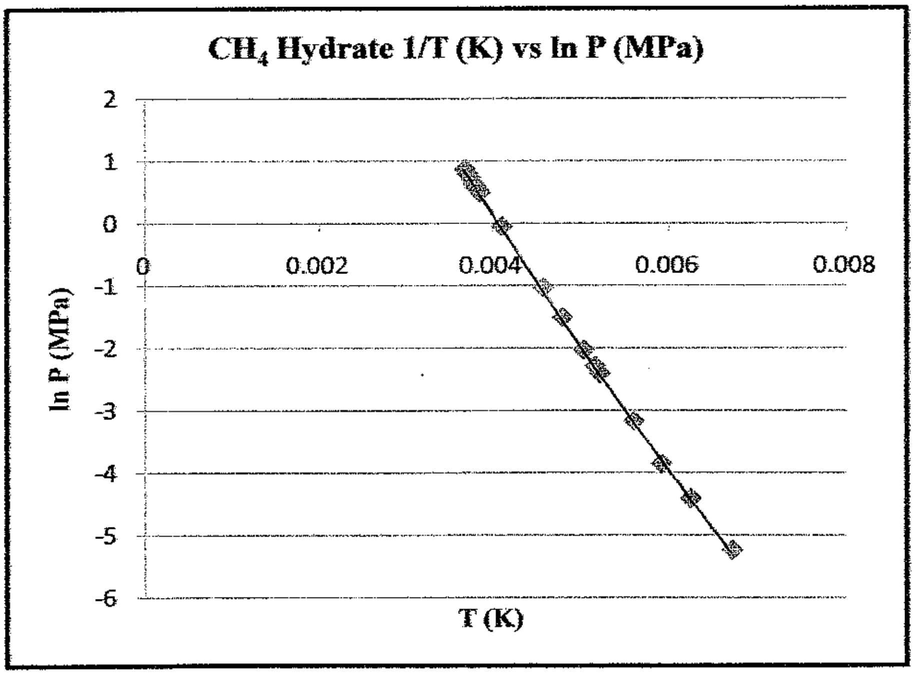

Figure 4.1: (p,T) data along the (ice, hydrate, vapor) coexistence line for methane hydrate, third order polynomial fit.

From the graph, the fit parameters for equation (12) and (13) can be represented in table 4.1 below:

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i(\frac{K}{T})^i \tag{12}$$

The function is differentiated with respect to 1/ *T* that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i(\frac{K}{T})^i \tag{13}$$

Table 4.1: Fitted parameters for determination of ΔH_2.

Parameter	**Value**
a_0	10.016
a_1	-2725.8
a_2	66998

The region for temperature is selected from 150 K to 270 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while d*p*/ d*T* calculated using equation (14).

$$\frac{dp}{dT} = \frac{-(p)}{T^2}\frac{d\ln(p)}{d(\frac{1}{T})}$$

(14)

In determining the volume changes for ΔH_2, the calculation has be shown in Chapter 3 where the changes of volume in methane vapor minus the volume of hydrate containing 1 mole methane is taken into account. ($\Delta V = V_{CH_4} - 2.739e^{-6}$ x *n*). The summary of data calculated is shown in Table 4.2.

Table 4.2: Enthalpy change for ΔH_2, from 150 K to 270 K.

T (K)	P (MPa)	dp/dT (MPa/ K)	ΔV_2 (m^3/ mol)	ΔH_2 (kJ/ mol)
150	0.00564	0.0004593	0.2212	15.24
170	0.02473	0.001651	0.057142	16.04
190	0.08421	0.004690	0.018742	16.70
210	0.2358	0.01111	0.007388	17.24
230	0.5662	0.02287	0.003361	17.68
250	1.203	0.04209	0.001711	18.01
270	2.315	0.07084	0.000953	18.23

4.1.2 Enthalpy of Dissociation of Clathrate Hydrate to Methane Vapor and Water (ΔH_{Ia} *and* ΔH_{Ib})

The equation that represents the dissociation of methane hydrate to water and methane vapor,

$$CH_4.nH_2O_{(s)} \rightarrow \left(1 - \frac{nxCH_4}{1-xCH_4}\right)CH_{4\,(g)} + nH_2O_{(l,\,CH_4\,sat)} \quad (\Delta H_{Ia}) \qquad (9)$$

The graph of (p,T) data plotted for ΔH_{Ia} is shown below:

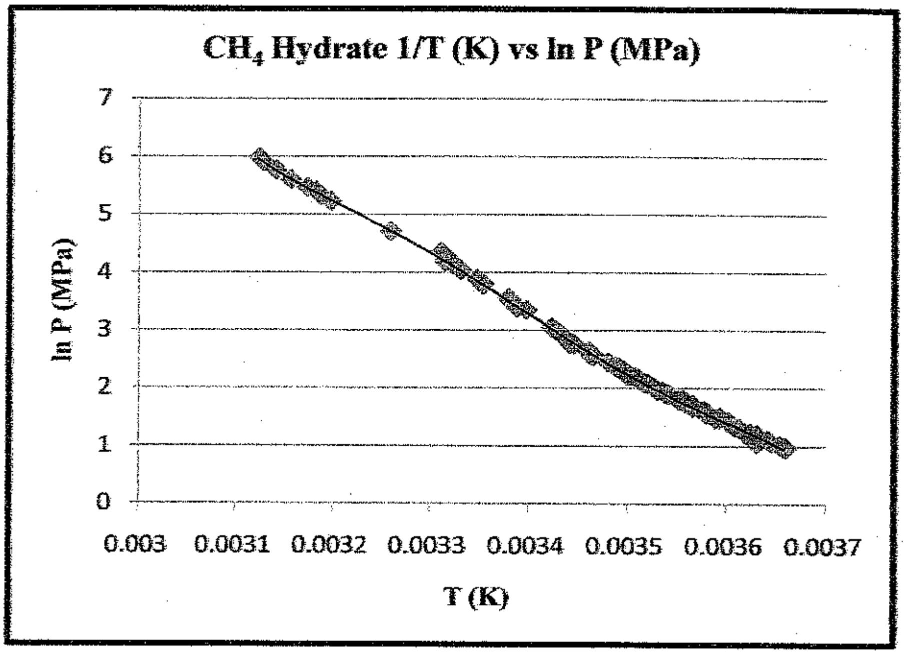

Figure 4.2: (p,T) data along the (liquid, hydrate, vapor) coexistence line for methane hydrate, sixth order polynomial fit.

From the graph, the fit parameters for equation (16) and (17) can be represented in table 4.3 below:

Table 4.3: Fitted parameters for determination of ΔH_{la}.

Parameter	Value
b_0	$1.86461e^{+05}$
b_1	$-2.75067e^{+08}$
b_2	$1.62155e^{+11}$
b_3	$-4.77455e^{+13}$
b_4	$7.02147e^{+15}$
b_5	$-4.12578e^{+17}$

The region for temperature is selected from 274 K to 318 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while dp/ dT calculated using equation (14). In determining the volume changes for ΔH_{Ia}, the calculation has be shown in Chapter 3 where $\Delta V_{Ia} = \left(1 - \frac{nxCH_4}{1-xCH_4}\right) V_{CH_4}$ (volume of n moles ice) + nV_{liq} (volume of 1 mole methane vapor) – V_{hyd} (volume of hydrate containing 1 mole methane is taken into account . The summary of data calculated is shown in Table 4.4.

Table 4.4: Enthalpy change for ΔH_{Ia}, from 274 K to 318 K.

T (K)	P (MPa)	dp/ dT (MPa/ K)	x_{CH_4}	ΔV_{Ia} (m^3/ mol)	ΔH_{Ia} (kJ/ mol)	ΔH_{Ib} (kJ/ mol)	ΔH_I (kJ/ mol)
274	2.85000	0.3209266	0.001046	0.000605	53.12	0.13274	53.25
278	4.28000	0.4172600	0.001455	0.00046	53.36	0.15852	53.52
282	6.36000	0.6635091	0.00181	0.000291	54.45	0.18425	54.63
286	9.88000	1.1519971	0.00229	0.000169	55.68	0.21729	55.90
290	16.06000	2.0111545	0.00286	0.0000915	53.37	0.25903	53.63
294	26.69000	3.3744460	0.00349	0.0000527	52.28	0.28753	52.57
298	43.92000	5.2755647	0.00419	0.0000339	53.29	0.29361	53.59
302	69.68000	7.5716436	0.00499	0.0000236	53.96	0.29416	54.26
306	105.18000	10.0970266	0.00583	0.0000175	54.07	0.26695	54.34
310	151.70000	13.1870032	0.00661	0.0000132	53.96	0.20002	54.16
314	214.40000	18.5766253	0.00723	0.00000929	54.19	0.08095	54.27
318	311.14000	31.2279381	0.00744	0.00000545	54.12	-0.11463	54.01

ΔH_{Ib} is calculated by calculations steps shown in Chapter 3, from equation 20 to 22. The table below summarizes the value calculated.

Table 4.5: Enthalpy change for ΔH_{1b}, from 274 K to 318 K.

T (K)	P (MPa)	x_{CH_4}	$V_{\infty CH_4,H_2O}(p-p^S)$ (kJ/mol)	$R\frac{d\ln K_H}{d(1/T)}$ (kJ/ mol)	$\Delta H_{\infty CH_4,H_2O}$	$\Delta H_{\infty 1b}$
274	2.85000	0.00105	0.0980	-19.313	-19.2150	0.13274
278	4.28000	0.00146	0.1490	-18.219	-18.0700	0.15852
282	6.36000	0.00181	0.2220	-17.157	-16.9350	0.18425
286	9.88000	0.00229	0.3460	-16.124	-15.7780	0.21729
290	16.06000	0.00286	0.5660	-15.618	-15.0520	0.25903
294	26.69000	0.00349	0.9450	-14.628	-13.6830	0.28753
298	43.92000	0.00419	1.5620	-13.192	-11.6300	0.29361
302	69.68000	0.00499	2.4910	-12.267	-9.7760	0.29416
306	105.18000	0.00583	3.7780	-11.365	-7.5870	0.26695
310	151.70000	0.00661	5.4770	-10.487	-5.0100	0.20002
314	214.40000	0.00723	7.7790	-9.6315	-1.8525	0.08095
318	311.14000	0.00744	11.3460	-8.7973	2.5487	-0.11463

4.1.3 Hydration Number of Clathrate Hydrate at Q1.

At quadruple point Q1, both reaction of (7) and (8) occur simultaneously. Subtracting reaction (8) from reaction (7),

$$n\,H_2O\,(l) \rightarrow n\,H_2O\,(s)$$

The quadruple point Q1 is not far removed from standard conditions where p = 0.1013 MPa and T = 273.15 K, and thus the enthalpy of fusion at Q1 will be very close to the standard enthalpy of fusion of ice, 6.01 kJ/ mol.

The most useful comparison of the present work is with the calorimetric study of Handa (1986) who reported values for ΔH_1 and ΔH_2 corrected to standard conditions of p = 0.1013 MPa and T = 273.1 K. Table 4.6 summarized all the known Clapeyron analyses to date for methane hydrate at Q1.

The accuracy test, AAD% is use to compare the value calculated in this work with the experimental value done by Handa (1986).

$$\text{AAD\%}_{\text{(average absolute deviation)}} = (x_{\text{experimental value}} - x_{\text{calculated}}) / x_{\text{experimental value}}$$

Table 4.6: Comparison of Clapeyron analyses for ΔH_1 and ΔH_2 at Q1.

Technique	**Source**	**ΔH_1 (kJ/mol)**	**ΔH_1 AAD %**	**ΔH_2 (kJ/mol)**	**ΔH_2 AAD%**	***n***	***n* AAD%**
Clapeyron	de Roo et al.	67.85	25.2	23.37	28.9	7.4	23.3
Clapeyron	Roberts et al.	54.36	0.31	19.06	5.13	5.87	2.17
Clapeyron	Deaton and Frost	55.12	1.72	-	-	-	-
Clapeyron	McLeod and Campbell	55.07	1.62	-	-	-	-
Clapeyron	Marshall et al.	53.41	1.44	-	-	-	-
Clapeyron	Yoon et al.	53.81	0.71	17.53	3.31	6.03	0.5
Clapeyron	Glew	55.36	2.16	18.06	0.38	6.2	3.33
Clapeyron	Anderson	52.9	2.38	17.47	3.6	5.9	1.67
Experimental	Handa	54.19	-	18.13	-	6	-
Clapeyron	**Present Work**	**53.23**	**1.77**	**18.24**	**0.61**	**5.82**	**3.0**

4.1.4 Discussion

Previous determinations of enthalpy of dissociation for methane hydrate have been done using the Clapeyron equation. However, almost all of these analysis have used the approximation leading to the Clausius – Clapeyron equation, namely the neglect of the volumes of the condensed phases. This approximation tends to overestimate the ΔV term in the Clapeyron equation and hence gives too large value for ΔH.

The enthalpies of dissociations ΔH_1 and ΔH_2 are in excellent agreement with the experimental results (Handa, 1986). The hydration number at Q1, $n = 5.82$, also agrees with that reported by Handa, $n = 6$. The other study of methane hydrate that attempts to calculate enthalpies and hydration numbers as a continuous function of temperature is the study of Glew (2002) and Anderson (2004). Their results for hydration number agree with the present results within experimental error over most of the temperature range.

Both results (Glew and Anderson) for the enthalpy of dissociation is between 5% to 10% larger than the present work calculated and it show a definite trend with temperature, in contrast to the present results. This comparison between the previous results and those of Glew and Anderson are unclear but might be due to differing methods for determining the molar volume of the hydrate.

Regardless of which result is closer to the truth, it is clear that the structure and energetic of methane hydrate have at most a small variation over a wide range of temperatures and pressures. This is a testament to the extraordinary stability of methane hydrate, which in turn no doubt derives from the fact that the methane molecule is a good fit to both small and large cages in the SI structure. Methane hydrate differs in this respect from carbon dioxide hydrate, for which a previous study shows that the cage filling varies significantly with temperature and pressure. (Anderson, 2003)

4.2 CARBON DIOXIDE HYDRATE

4.2.1 Enthalpy of Dissociation of Clathrate Hydrate to Carbon Dioxide Vapor and Ice (ΔH_2)

The graph of (p,T) data plotted for ΔH_2 is shown below:

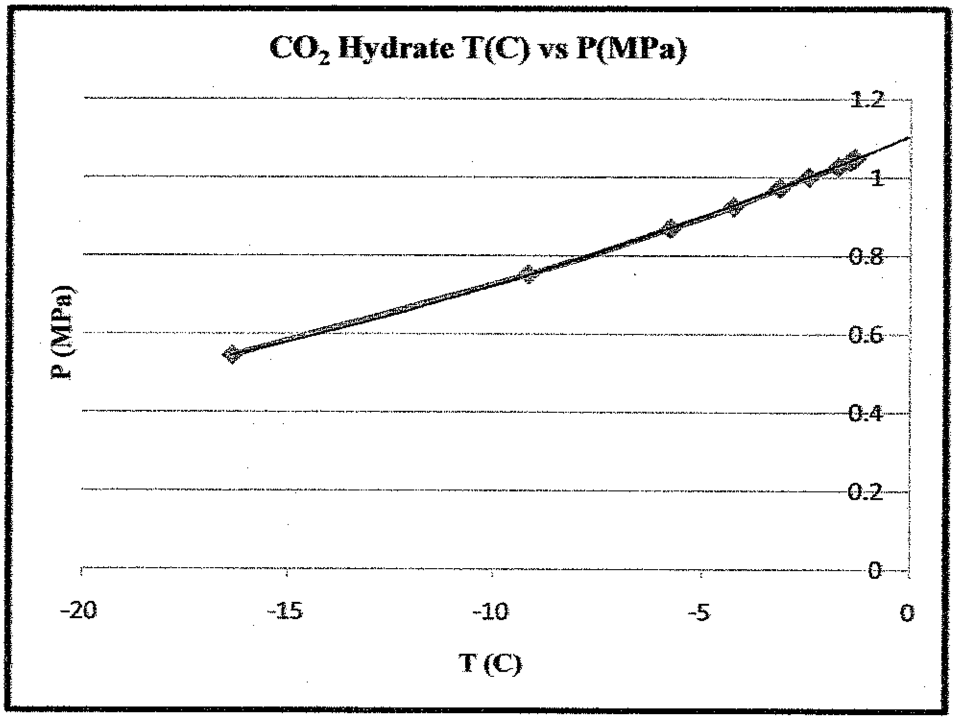

Figure 4.3: (p,T) data along the (ice, hydrate, vapor) coexistence line for carbon dioxide hydrate, third order polynomial fit.

From the graph, the fit parameters for equation (12) and (13) can be represented in table 4.7 below:

Table 4.7: Fitted parameters for determination of ΔH_2.

Parameter	Value
a_0	1.1046
a_1	0.04449
a_2	0.000629

The region for temperature is selected from 259.15 K to 271.15 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while dp/dT calculated using equation (14). In determining the volume changes for ΔH_2, the calculation only takes into account the changes of volume in carbon dioxide vapor. ($\Delta V = V_{CO_2}$). The summary of data calculated is shown in Table 4.8.

Table 4.8: Enthalpy change for ΔH_2, from 259.15 K to 271.15 K.

T (K)	**P (MPa)**	**dp/dT (MPa/ K)**	**ΔV_2 (CO_2) (m^3/ mol)**	**ΔH_2 (kJ/ mol)**
259.15	0.605	0.02688	3.385	23.58
260.15	0.632	0.02814	3.245	23.75
261.15	0.661	0.02939	3.11	23.87
262.15	0.691	0.03065	2.98	23.95
263.15	0.723	0.03191	2.856	23.98
264.15	0.755	0.03317	2.738	23.99
265.15	0.789	0.03443	2.625	23.96
266.15	0.824	0.03568	2.518	23.91
267.15	0.86	0.03694	2.415	23.83
268.15	0.898	0.03820	2.317	23.73
269.15	0.937	0.03946	2.224	23.62
270.15	0.977	0.04072	2.136	23.49
271.15	1.018	0.04197	2.052	23.35

4.2.2 Enthalpy of Dissociation of Clathrate Hydrate to Carbon Dioxide Vapor and Water (ΔH_{1a} and ΔH_{1b})

The graph of (p,T) data plotted for ΔH_{1a} is shown below:

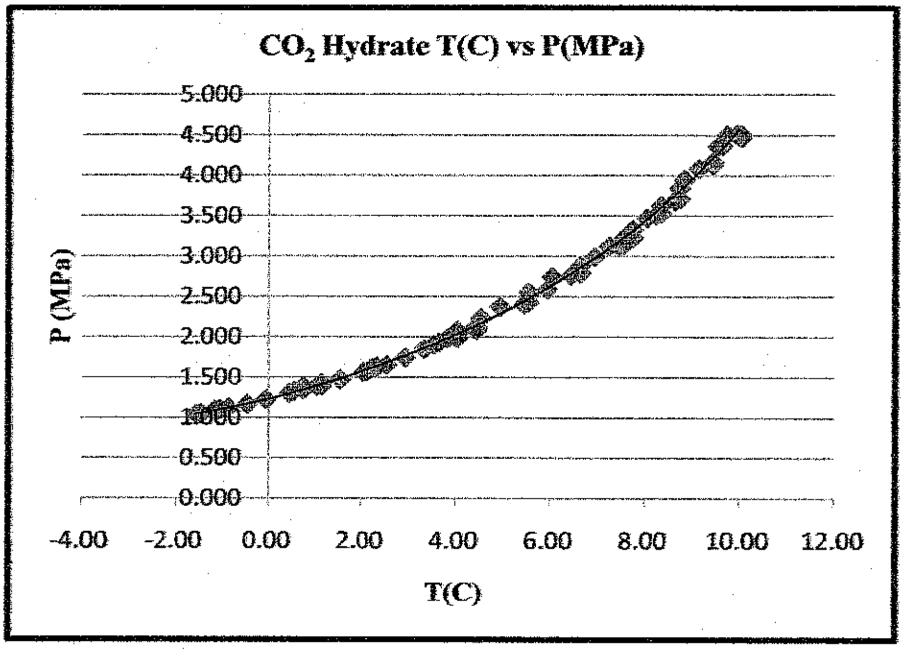

Figure 4.4: (p,T) data along the (liquid, hydrate, vapor) coexistence line for carbon dioxide hydrate, fifth order polynomial fit.

From the graph, the fit parameters for equation (16) and (17) can be represented in table 4.9 below:

Table 4.9: Fitted parameters for determination of ΔH_{1a}.

Parameter	Value
b_0	1.2242
b_1	0.14119
b_2	0.014872
b_3	-0.0005674
b_4	0.0000972

The region for temperature is selected from 274.15 K to 282.15 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while d*p*/ d*T* calculated using equation (14). In determining the volume changes for

ΔH_{Ia}, the calculation has be shown in Chapter 3 where $\Delta V_{Ia} = \left(1 - \frac{nxCO_2}{1-xCO_2}\right) V_{CO2}$ (volume of n moles ice) + nV_{liq} (volume of 1 mole carbon dioxide vapor) – V_{hyd} (volume of hydrate containing 1 mole carbon dioxide is taken into account . The summary of data calculated is shown in Table 4.10.

Table 4.10: Enthalpy change for ΔH_{Ia}, from 274.15 K to 282.15 K.

T (K)	P (MPa)	x_{CO_2}	dp/dT (MPa/ K)	ΔV (m^3/ mol)	ΔH_{Ia} (kJ/ mol)	ΔH_{Ib} (kJ/ mol)	ΔH_I (kJ/ mol)
274.15	1.380	0.0162	0.1696	0.001371	63.62	2.256	65.88
275.15	1.563	0.0174	0.1970	0.001193	64.36	2.426	66.79
276.15	1.774	0.0187	0.2256	0.001035	63.89	2.610	66.50
277.15	2.015	0.0200	0.2578	0.000896	63.08	2.796	65.87
278.15	2.292	0.0214	0.296	0.000773	62.25	2.995	65.24
279.15	2.610	0.0228	0.342	0.000662	61.57	3.196	64.76
280.15	2.980	0.0244	0.399	0.000561	60.85	3.426	64.27
281.15	3.413	0.0261	0.469	0.000468	59.94	3.671	63.61
282.15	3.923	0.0279	0.554	0.000383	58.59	3.931	62.52

ΔH_{Ib} reaction represents the formation of a saturated solution of CO_2 in water, at a pressure corresponding to the (liquid, hydrate, vapor) phase boundary at a given temperature. The reaction is non-stoichiometric that xCO_2 varies with temperature and pressure and therefore so does the enthalpy change due to reaction. However, the solubility of CO_2 is low such that the mole fraction xCO_2 does not exceed 0.03 in the hydrate-forming region. Therefore, the enthalpy of solution at infinite dilution for CO_2 in water can be used with little error. This value ($\Delta H^{\infty}_{(CO_2,\ H_2O)}$ = - 22.83 kJ/ mol) has been determined from recent measurement by Anderson (2002). $\Delta H_{Ib} = (22830\ nx(CO_2))/\ (1 - x(CO_2))$ where n = 6. The table below summarizes the value calculated at given temperature and pressure.

Table 4.11: Enthalpy change for ΔH_{1b}, from 274.15 K to 282.15 K.

T (K)	P (MPa)	x_{CO_2}	ΔH_{1b} (kJ/ mol)
274.15	1.380	0.0162	2.256
275.15	1.563	0.0174	2.426
276.15	1.774	0.0187	2.610
277.15	2.015	0.0200	2.796
278.15	2.292	0.0214	2.995
279.15	2.610	0.0228	3.196
280.15	2.980	0.0244	3.426
281.15	3.413	0.0261	3.671
282.15	3.923	0.0279	3.931

4.2.3 Hydration Number of Clathrate Hydrate at Q1.

At quadruple point Q1, both reaction of (7) and (8) occur simultaneously. Subtracting reaction (8) from reaction (7),

$$n\,H_2O\,(l) \rightarrow n\,H_2O\,(s)$$

The quadruple point Q1 is not far removed from standard condition $T = 271.8$ K, and thus the enthalpy of fusion at Q1 will be very close to the standard enthalpy of fusion of ice, 6.01 kJ/ mol.

The most useful comparison of the present work is with the differential scanning calorimetric study of Kang *et. al* (2001) who reported values for ΔH_1 and ΔH_2 at Q1 is 65.22 kJ/ mol and 21.77 kJ/ mol. Table x summarized all the known Clapeyron analyses to date for methane hydrate at Q1.

The accuracy test, AAD% is use to compare the value calculated in this work with the experimental value done by Kang *et. al.* (2001).

$$\text{AAD\%}_{\text{ (average absolute deviation)}} = (x_{\text{ experimental value}} - x_{\text{ calculated}}) / x_{\text{ experimental value}}$$

Table 4.12: Comparison of previous analyses for ΔH_1 and ΔH_2 at Q1.

Technique	**Source**	**Δ H$_1$ (kJ/mol)**	**Δ H$_1$ AAD %**	**Δ H$_2$ (kJ/mol)**	**Δ H$_2$ AAD%**	***n***	***n* AAD%**
Clausius-Clapeyron	Larson	60.2	7.69	-	-	-	-
Clausius-Clapeyron	Bozzo *et al.*	58.99	9.55	-	-	-	-
Clausius-Clapeyron	Vlahakis *et al.*	59.9	10.8	-	-	-	-
Clausius-Clapeyron	Long	73	8.16	-	-	-	-
Clausius-Clapeyron	Kamath	80.1	11.9	-	-	-	-
Clausius-Clapeyron	Yoon *et al.*	57.66	2.28	-	-	-	-
Clapeyron	Anderson	63.6	2.48	23.93	9.92	6.6	8.71
Experimental	Kang *et. al.*	65.22	-	21.77	-	7.23	-
Clapeyron	**Present Work**	66.02	**1.23**	**23.58**	**8.31**	7.1	**1.79**

4.2.4 Discussion

The first thing to note about table 4.12 is that in most cases there is single entry for ΔH_1 and/ or *n*. In some cases the measurement technique only gives a value at a single point. In other cases there is an assumption that ΔH_1 *and n* are constant, and thus analysis gives an average value. This is particularly true of the previous analyses using the Clausius-Clapeyron equation.

Previous determinations of ΔH_1 using the Clausius-Clapeyron equation have yielded varying results. Some of the reasons have been addressed earlier in this work. The results of Long and Kamath are unreasonably large in magnitude. The present work agrees most closely with Larson and Vlahakis *et. al.* whose values are very close to the average of present results at Q1 and Q2.

Yoon *et. el.* correctly noted the various assumptions that are often made in using the Clausius-Clapeyron equation for clathrate hydrates. They give approximate ranges for the errors that can arrive from each of the assumptions.

They do not provide enough details to evaluate their results. Also, it is unclear why "fixing" the Clausius-Clapeyron equation is preferable to using the simple Clapeyron equation directly.

Kang *et. al.* using experimental procedure, report a value of $\Delta H_1 = 65.22$ kJ/ mol for a hydrate sample that was prepared at T = 271.8 K, which agrees with present result $\Delta H_1 = 66.02$ k/ mol at that temperature. Experimental measurements are usually preferred over the Clapeyron equation analysis technique since experimental procedure is more "direct".

The present work suggest that the range of values for the hydration number is consistent with the idea that complete occupancy of the small cages in the SI structure can only occur at sufficiently high pressure. The Clapeyron equation is directly preferred to the use of the Clausius-Clapeyron equation for determining the enthalpy of dissociation of clathrate hydrates.

4.3 ETHANE HYDRATE

4.3.1 Enthalpy of Dissociation of Clathrate Hydrate to Ethane Vapor and Ice (ΔH_2)

The graph of (p,T) data plotted for ΔH_2 is shown below:

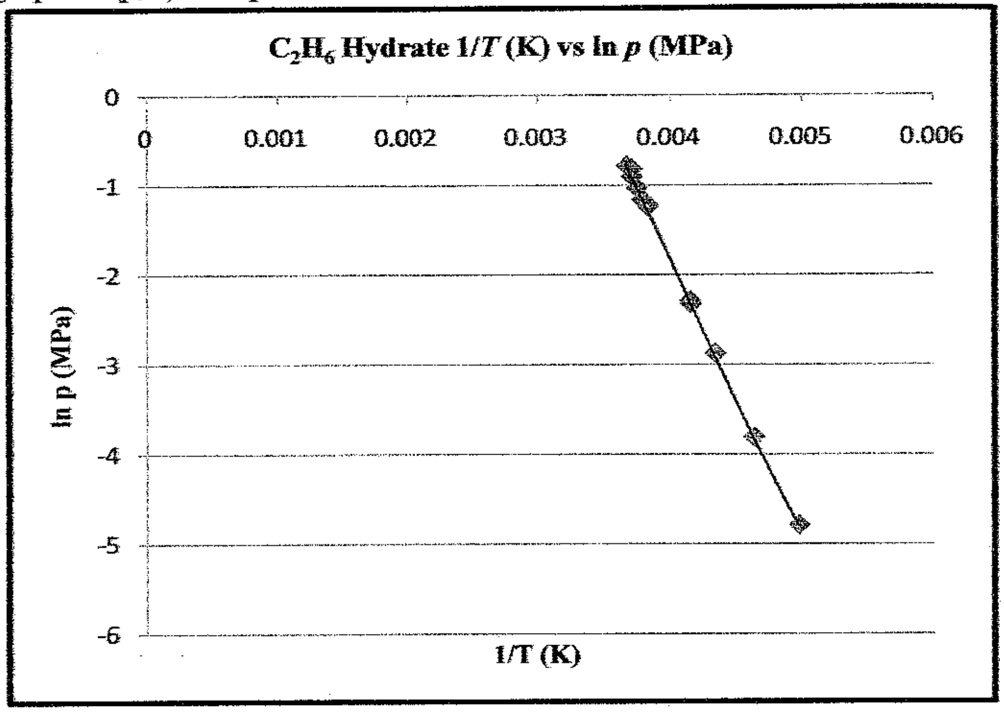

Figure 4.5: (p,T) data along the (ice, hydrate, vapor) coexistence line for ethane hydrate, fourth order polynomial fit.

From the graph, the fit parameters for equation (12) and (13) can be represented in table 4.13 below:

Table 4.13: Fitted parameters for determination of ΔH_2.

Parameter	Value
a_0	-7.95
a_1	$1.06e^{-4}$
a_2	$-3.35e^{-6}$
a_3	$2.70e^{+8}$

The region for temperature is selected from 190 K to 270 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while d*p*/ d*T* calculated using equation (14). In determining the volume changes for ΔH_2, the calculation has be shown in Chapter 3 where the changes of volume in ethane vapor minus the volume of hydrate containing 1 mole ethane is taken into account, similar to methane hydrate. ($\Delta V = V_{C2H6} - 2.739e^{-6} \times n$). The summary of data calculated is shown in Table 4.14.

Table 4.14: Enthalpy change for ΔH_2, from 190 K to 270 K

T(K)	P(MPa)	d*p*/d*T* (MPa/ K)	ΔV (C_2H_6) (m^3/ mol)	ΔH_2 (kJ/ mol)
190	0.004238	$2.578E^{-04}$	0.373	18.26
200	0.008007	$5.245E^{-04}$	0.208	21.79
210	0.01549	$1.022E^{-03}$	0.1127	24.17
220	0.02969	$1.895E^{-03}$	0.0616	25.68
230	0.05528	$3.333E^{-03}$	0.0346	26.51
240	0.09892	$5.539E^{-03}$	0.0202	26.80
250	0.1692	$8.697E^{-03}$	0.0123	26.67
260	0.2764	$1.292E^{-02}$	0.0078	26.21
270	0.4311	$1.819E^{-02}$	0.0052	25.49

4.3.2 Enthalpy of Dissociation of Clathrate Hydrate to Ethane Vapor and Water (ΔH_{1a} and ΔH_{1b})

The graph of (p,T) data plotted for ΔH_{1a} is shown below:

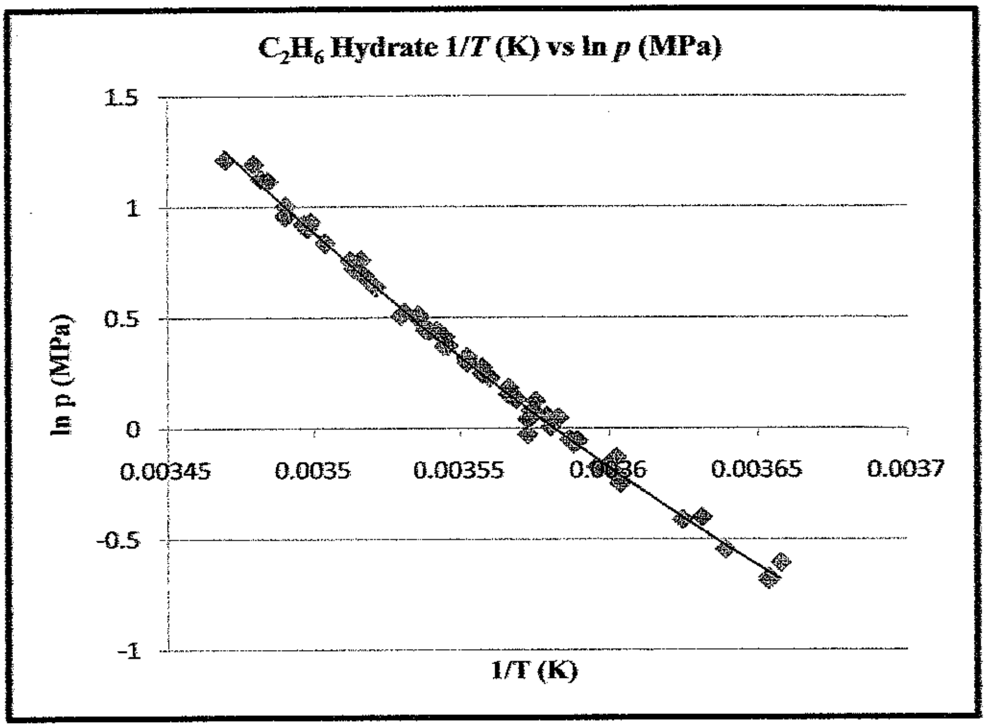

Figure 4.6: (p,T) data along the (liquid, hydrate, vapor) coexistence line for ethane hydrate, third order polynomial fit.

From the graph, the fit parameters for equation (16) and (17) can be represented in table 4.15 below:

Table 4.15: Fitted parameters for determination of $\Delta H_{1\alpha}$.

Parameter	Value
b_0	$1.872e^{+02}$
b_1	$-9.4e^{+04}$
b_2	$1.18e^{+07}$

The region for temperature is selected from 274 K to 290 K in calculating the enthalpy of dissociation. The pressure can be calculated directly from equation (12) while d*p*/ d*T* calculated using equation (14). In determining the volume changes for $\Delta H_{1\alpha}$, the calculation has be shown in Chapter 3 where $\Delta V_{1\alpha} = \left(1 - \frac{nxC_2H_6}{1-xC_2H_6}\right) V_{CH_4}$ (volume of n moles ice) + nV_{liq} (volume of 1 mole ethane vapor) – V_{hyd} (volume of hydrate containing 1 mole ethane is taken into account. The summary of data calculated is shown in Table 4.16.

Table 4.16: Enthalpy change for ΔH_{1a}, from 274 K to 290 K.

T(K)	P (MPa)	dp/ dT (MPa/ K)	x_{C2H6}	ΔV_{1a} (m^3/ mol)	ΔH_{1a} (kJ/ mol)	ΔH_{1b} (kJ/ mol)	ΔH_1 (kJ/ mol)
274	0.5742	0.06325	0.001455	0.00046	72.24	0.29361	72.54
278	0.9158	0.11272	0.00229	0.000169	73.04	0.26695	73.31
282	1.5345	0.20684	0.00349	0.0000527	73.96	0.25903	74.22
286	2.6884	0.39088	0.00499	0.0000236	74.65	0.22281	74.87
290	4.9038	0.75999	0.00661	0.0000132	73.54	0.1989	73.74

ΔH_{Ib} is calculated by calculations steps shown in Chapter 3, from equation 20 to 22. The table below summarizes the value calculated.

Table 4.17: Enthalpy change for ΔH_{Ib}, from 274 K to 290 K.

T (K)	P (MPa)	x_{C2H6}	$V_{\infty C2H6,H2O}(p-p^S)$ (kJ/mol)	$R\frac{d\ln K_H}{d(1/T)}$ (kJ/ mol)	$\Delta H_{\infty C2H6,H2O}$	$\Delta H_{\infty 1b}$
274	0.5742	0.001455	0.2220	-19.313	-19.2150	0.29361
278	0.9158	0.00229	0.3412	-18.219	-18.0700	0.26695
282	1.5345	0.00349	0.5661	-17.157	-16.9350	0.25903
286	2.6884	0.00499	0.773	-16.124	-15.7780	0.22281
290	4.9038	0.00661	0.3362	-15.618	-15.0520	0.1989

4.3.3 Hydration Number of Clathrate Hydrate at Q1.

At quadruple point Q1, both reaction of (7) and (8) occur simultaneously. Subtracting reaction (8) from reaction (7),

$$n\,H_2O\,(l) \rightarrow n\,H_2O\,(s)$$

The quadruple point Q1 is not far removed from standard conditions where T = 273.15 K, and thus the enthalpy of fusion at Q1 will be very close to the standard enthalpy of fusion of ice, 6.01 kJ/ mol.

The most useful comparison of the present work is with the calorimetric study of Handa (1986) who reported values for ΔH_1 and ΔH_2 corrected to standard conditions of $T = 273.15$ K. Table x summarized the comparison value in present work with Handa for ethane hydrate at Q1.

The accuracy test, AAD% is use to compare the value calculated in this work with the experimental value done by Handa (1986).

$$\text{AAD\%}_{\text{(average absolute deviation)}} = (x_{\text{experimental value}} - x_{\text{calculated}}) / x_{\text{experimental value}}$$

Table 4.18: Comparison of Clapeyron analyses for ΔH_1 and ΔH_2 at Q1.

Technique	**Source**	**Δ H₁ (kJ/mol)**	**Δ H₁ AAD %**	**Δ H₂ (kJ/mol)**	**Δ H₂ AAD%**	***n***	***n* AAD%**
Experimental	Handa	71.8	-	25.7	-	7.67	-
Clapeyron	**Present Work**	**72.51**	**0.97**	**25.31**	**1.52**	7.85	**2.35**

4.3.4 Discussion

The only comparison can be made is between present work with the experimental result done by Handa. The result calculated is agree to be closed with the experimental value which gives approximately 1% error for both value. Since there is no comparison can be made by using the Clapeyron equation with previous study, it can be assume that the Clapeyron equation will give accurate results when calculation is made.

The method outlined by Anderson (2003, 2004) to calculate the enthalpy of dissociation and hydration number is proved to work extremely well. When comparison is made, the results calculated were close with the experimental work indicates that the Clapeyron equation is the good in determination of enthalpies.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Method for determining the enthalpy of dissociation of clathrate hydrates using the Clapeyron equation which takes into account the solubility of gases in water and the non – ideality of vapor phases. To fully exploit the rigor of the Clapeyron equation, a large amount of supplemental data for hydrate systems is required.

For methane hydrate, when comparison is made between experimental values with present work calculated, the AAD% for ΔH_1 is 1.77% and ΔH_2 is 0.61% where the error can be concluded as low. For hydration number the AAD% is 3.0% which is estimated closer to the experimental value.

For carbon dioxide hydrate, when comparison is made between experimental values with present work calculated, the AAD% for ΔH_1 is 1.23% and ΔH_2 is 8.31% where the error can be concluded as low. For hydration number the AAD% is 1.79% which is estimated closer to the experimental value.

For ethane hydrate, when comparison is made between experimental values with present work calculated, the AAD% for ΔH_1 is 0.97% and ΔH_2 is 1.52% where the error can be concluded as low. For hydration number the AAD% is 2.35% which is estimated closer to the experimental value.

The present study does not completely resolve the problems occurred when determining the enthalpy of dissociation and hydration number. However, from this project it can be concluded that the Clapeyron equation is better when comparison is made between the Clausius – Clapeyron equation with experimental studies.

The net result yielded a very satisfactory analysis whose results are in accord with almost all previous studies. For most other clathrate hydrates, which exist at different pressures than the clathrate hydrates that is studied in this work, the method outlined in this project is also expected to work extremely well.

5.2 RECOMMENDATION

After analyzing the calculated result for three different types of clathrate hydrates with the same methodology which is using the Anderson (2004) analysis, it yield the result that have relatively small error when comparison is made with the experimental data. Thus, in the future, the same methodology can be applied to determine enthalpy of dissociation and hydration number for mixed clathrate hydrates systems.

The experimental result is assumed as the accurate since it involves the real application. Thus, conducting an experimental procedure to calculate the enthalpy of dissociation and hydration number will yield true result where comparison can be made with the estimated result from the Clapeyron equation.

REFERENCES

Adewumi, M., (2008). The Hydrate Problem: PNG520: Phase Behavior of Natural Gases & Condensate Fluids, Module Engineering Applications (II), https://www.e-education.psu.edu/png520/m21_p3.html, 3rd March 2010.

Anderson, G.K., (2002). J. Chem. Eng. Data, 47, pp 219-222.

Anderson, G.K., (2003). J. Chem. Thermodyn, 35 (7), pp 1171-1183.

Anderson, G.K., (2004). J. Chem. Thermodyn, 36 (12), pp 1119-1127.

Benson, B.B. and Krause D. Jr., (1989). J Sol. Chem., 18 (9), pp 803-821.

Buffett, B. and Archer, D., (2004). *Earth Planet*, 127, pp 183-194

Caroll, J., (2003). *Natural gas hydrates*, 1st Edition, Penwell Books Publication.

Chatti, I., Delahaye, A., Fournaison, L. and Petitet, J.P., (2005). J. Econman, 46 (9-10), pp 1333-1343.

Delahaye, A. *et. al.*, (2006). Ind. Eng. Chem. Res., 45, pp 391–397.

Dhima, A., De Hemptinne, J.-C. and Jose, J., (1999). Ind. and Eng. Chem. Res., 38 (8), pp 3144-3161.

Fournaison, L., Delahaye, A., Chatti I. and Petitet, J.P., (2004). Ind Eng Chem Res, 43 (20), pp 6521–6526.

Glasby, G.P., (2003). Mar Petrol Geol, 20 (2), pp 163–175.

Hammerschmidt, E.G., (1934). Ind. Eng. Chem., 26 (8), pp 851-855.

Handa Y.P., (1986). J. Chem. Thermodyn., 18, pp 915-921.

Kang, S.P., Lee, H., Ryu, B.J.. (2001). J. Chem. Thermodyn., 33, pp 513-521.

Krichevsky, I.R. and Kasarnovsky, J.S., (1935). J. Am. Chem. Soc., 57 (11), pp 2168-2171.

Kyle, B.G., (1999). *Chemical and process thermodynamics,* 3rd edition, Prentice Hall, US.

Lee, S., Liang, L., Riestenberg, D., West, O.R., Tsouris, C. and Adams, E., (2003). Environ Sci Technol, 37 (16), pp 3701–3708.

Makogon, Y.F., (1997). *Hydrates of hydrocarbons,* 1st Edition, Texas A&M University.

Price, G., (1998). *Thermodynamics of chemical processes,* 2nd Edition, Oxford University Press, London.

Rettich, T.R., Handa, Y.P., Battino, R. and Wilhelm, E., (1981). J. Phys. Chem., 85 (22), pp 3230-3237.

Sabil, K.M., (2009). *Phase behavior, thermodynamics and kinetics of clathrate hydrate systems of carbon dioxide and electrolytes,* 1st Edition, CPI Wohrmann Print Service.

Servio, P. and Englezos, P., (2002). J. Chem. Eng. Data, 47 (1), pp 87-90.

Sloan, E.D. Jr. and Koh, C.A., (2003). *Clathrate Hydrates of Natural Gases*, 3rd Edition, Marcel &Dekker, New York.

Sloan, E.D. Jr., (2000). Ind Eng Chem Res, 39 (9), pp 3123–3129.

Sloan, E.D. Jr., (2000). *Hydrate Engineering*, monograph volume 21.

Sloan, E.D. Jr., (2003). J. Chem Thermodyn, 426 (6964), pp 353-359.

Tanasawa, I. and Takao, S., (2002). Low-temperature storage using clathrate hydrate slurries of tetra-n-butylammonium bromide: thermophysical properties and morphology of clathrate hydrate crystal, Fourth international conference on gas hydrates. Yokohama, Japan, pp 963–967.,

Thomas, E., (2004). *Clathrate: little known components of a global carbon cycle*, Wesleyan University.

Weast, Robert, C., (1981). *Handbook of Chemistry and Physics,* 61st Edition, CRC Publication, Florida.

APPENDIX I:

Calculation Steps of Enthalpy of Dissociation:

Carbon Dioxide Hydrate

The enthalpy of dissociation of carbon dioxide hydrate will be determined from the two equations represent the dissociation of:

- Carbon dioxide hydrate to liquid water & gaseous carbon dioxide.

$$CO_2.nH_2O_{(s)} \rightarrow CO_{2\,(g)} + nH_2O_{(l)} \qquad (\Delta H_1) \qquad (7)$$

- Carbon dioxide hydrate to ice water & gaseous carbon dioxide.

$$CO_2.nH_2O_{(s)} \rightarrow CO_{2\,(g)} + nH_2O_{(s)} \qquad (\Delta H_2) \qquad (8)$$

Determination of ΔH_1 and ΔH_2 will be done from an analysis of the pressure and temperature (p, T) behavior along the liquid, hydrate, vapor (L, H, V) and ice, hydrate, vapor (I, H, V) equilibrium lines respectively.

According to Anderson (2004), there is a small complication with regard to reaction for ΔH_1, the liquid in equilibrium with hydrate is not pure water, and rather it is water that is saturated with respect to carbon dioxide at the appropriate temperature and pressure.

The mole fraction of carbon dioxide in the water in equilibrium with the hydrate is x_{CO_2}. Then n moles of water supplies $nx_{CO_2} / (1 - x_{CO_2})$ moles of carbon dioxide to the hydrate; while the rest is comes from the gas. Thus, reaction for ΔH_1 must be analyzed as the sum of two terms:

$$CO_2.nH_2O_{(s)} \rightarrow \left(1 - \frac{nxCO_2}{1-xCO_2}\right) CO_{2\,(g)} + n\,H_2O_{\,(l,\,CO_2\,sat)} \qquad (\Delta H_{1a})$$

(9)

$$CO_2.nH_2O_{(s)} \rightarrow \left(\frac{nxCO_2}{1-xCO_2}\right) CO_{2\,(g)} + n\,H_2O_{\,(l)} \qquad (\Delta H_{1b})$$

(10)

The term H_2O (l, CO_2 sat) refers to a mole of liquid water which is saturated with respect to carbon dioxide at the given temperature and pressure. The Clapeyron equation will be used to find ΔH_{1a}, while solubility data will be used to find ΔH_{1b}. For ΔH_2, enthalpy can be determined directly because solubility of carbon dioxide in ice is negligible.

The Clapeyron equation is presented without derivation gives;

$$\Delta H = T\,\Delta V\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)$$

(11)

From there, the analysis begins with the determination of ΔH_2 because is it straightforward and the value of ΔH_2 will be used in order to find ΔH_1 and n.

The (p, T) of three phase equilibrium (ice, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Larson (1955)

The (p, T) data will be plotted as ln (p/ MPa) vs. K/T graph. Then, the graph will be least-squares fitted to a third order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_2 will be calculated manually while; the dp/ dT will be calculated using the equilibrium graph plotted before. Based on the graph, the dp/ dT can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i(\frac{K}{T})^i \tag{12}$$

The function is differentiated with respect to 1/ T that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i(\frac{K}{T})^i \tag{13}$$

Finally, dp/ dT at each temperature and pressure is found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2}\frac{\mathrm{d}\ln(p)}{\mathrm{d}(\frac{1}{T})} \tag{14}$$

The fitted parameters of b_0, b_1 and b_2 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_2. ΔV_2 is equal to;

n V_{ice} (volume of n moles ice) + V_{CO_2} (volume of 1 mole carbon dioxide vapor) – V_{hyd} (volume of hydrate containing 1 mole carbon dioxide).

(15)

The parameters for each sections of volume can be obtained from the data collected by previous studies and NIST webbook. From there, the Clapeyron equation for ΔH_2 can be easily calculated once the value for ΔV_2 and dp/ dT has been determined for selected temperature and pressure.

The next step is to determine the ΔH_1, we starts with ΔH_{1a}.

The (*p*, *T*) of three phase equilibrium (liquid, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Deaton and Frost (1946)
- Unruh and Katz (1949)
- Robinson and Mehta (1971)
- Ng and Robinson (1985)
- Vlahakis *et al.* (1972)
- Adisasmito *et al.* (1991)

The (*p*, *T*) data will be plotted as ln (*p*/ MPa) vs. *K*/T graph. Then, the graph will be least-squares fitted to a fifth order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_{1a} will be calculated manually while; the d*p*/ d*T* will be calculated using the equilibrium graph plotted before. Based on the graph, the d*p*/ d*T* can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i (\frac{K}{T})^i \tag{16}$$

The function is differentiated with respect to 1/ *T* that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i (\frac{K}{T})^i \tag{17}$$

Finally, d*p*/ d*T* at each temperature and pressure is found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2} \frac{\mathrm{d}\ln(p)}{\mathrm{d}\,(\frac{1}{T})} \tag{18}$$

The fit parameters of b_0, b_1, b_2, b_3, b_4 and b_5 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_{1a}. ΔV_{1a} is equal to;

$\left(1 - \frac{nxCO_2}{1-xCO_2}\right)$ V_{CH4} (volume of n moles ice) + nV_{liq} (volume of 1 mole carbon dioxide vapor) – V_{hyd} (volume of hydrate containing 1 mole carbon dioxide).

(19)

The parameters for each sections of volume can be obtained from the data collected by previous studies. Each of the sections will be determined according to the function. From there, the Clapeyron equation for ΔH_{1a} can be easily calculated once the value for ΔV_{1a} and dp/dT has been determined for selected temperature and pressure.

ΔH_{1b} can determined from the solubility data. The solubility can be evaluated by the available data using the Krichevsky-Kasarnorvsky (1935) equation;

$$\ln\left(\frac{f}{x_{CO_2}}\right) = \ln K_H + \frac{V\infty_{CO2,H2O}\,(p - p^s)}{RT}$$

(20)

Where f, fugacity of CO_2 in the gas phase; x_{CO2}, mole fraction of CO_2 dissolved in the liquid phase; K_H, Henry's law constant; $V\infty_{CO2,H2O}$, partial molar volume of CO_2 in water at infinite dilution; p, total system pressure; p^s, vapor pressure of water at temperature T.

The partial molar volume, $V\infty_{CO2,H2O}$ at infinite dilution is independent of pressure and slightly dependent of temperature and can be determined by;

$$ln\ \left[V\infty_{CO2,H2O}/(\mathrm{m}^3.\mathrm{mol}^{-1}\right] = -10.275 + 1.23 \times 10^{-3}\left(\frac{\mathrm{T}}{K} - 273.15\right)$$

(21)

The carbon dioxide solubility is found from the measured value from Servio and Englezos (2002). Because of the mole fraction x_{CO2} is so low, the enthalpy of solution per mole of carbon dioxide can be equated with little error to the partial molar enthalpy of solution at infinite dilution which denoted by$\Delta H\infty_{CO2,H2O}$.

Based on Benson and Krause (1989), $\Delta H\infty_{CO2,H2O}$ can be known by equation;

$$\Delta H\infty_{CO2,H2O} = R\frac{dln\,K_H}{d(\frac{1}{T})} - T\frac{dV\infty_{CO2,H2O}}{dT}(p-p^s) + V\infty_{CO2,H2O}(p-p^s) + TV\infty_{CO2,H2O}(\frac{dp^s}{dT}) \tag{22}$$

The second term in equation is negligible since $V\infty_{CO2,H2O}$ is almost independent of *T*. also, the fourth term is negligible due to the smallness of the water vapor pressure at the temperatures of hydrate formation. Once calculated, the $\Delta H1_b$ can be determined just by simply multiply the expression of $\Delta H\infty_{CO2,H2O}$ with the$\left(-\frac{nxCO_2}{1-xCO_2}\right)$.

Finally, the enthalpy of dissociation of carbon dioxide hydrate ΔH_l can be known by, the total submission of $\Delta H_{la} + \Delta H_{lb}$. For the calculation of hydration number can only be done once the enthalpy of both reactions has been determined.

The difference between enthalpy of both reactions will be divided with the enthalpy of fusion of water and the hydration number can be known.

Calculation Steps of Enthalpy of Dissociation:

Ethane Hydrate

The enthalpy of dissociation of ethane hydrate will be determined from the two equations represent the dissociation of:

- Ethane hydrate to liquid water & gaseous ethane.

$$C_2H_6.nH_2O_{(s)} \rightarrow C_2H_6\,_{(g)} + nH_2O_{(l)} \qquad (\Delta H_1) \tag{7}$$

- Ethane hydrate to ice water & gaseous ethane.

$$C_2H_6.nH_2O_{(s)} \rightarrow C_2H_6\,_{(g)} + nH_2O_{(s)} \qquad (\Delta H_2) \tag{8}$$

Determination of ΔH_1 and ΔH_2 will be done from an analysis of the pressure and temperature (p, T) behavior along the liquid, hydrate, vapor (L, H, V) and ice, hydrate, vapor (I, H, V) equilibrium lines respectively.

According to Anderson (2004), there is a small complication with regard to reaction for ΔH_1, the liquid in equilibrium with hydrate is not pure water, and rather it is water that is saturated with respect to ethane at the appropriate temperature and pressure.

The mole fraction of ethane in the water in equilibrium with the hydrate is $x_{C_2H_4}$. Then n moles of water supplies $nx_{C_2H_6} / (1 - x_{C_2H_6})$ moles of ethane to the hydrate; while the rest is comes from the gas. Thus, reaction for ΔH_1 must be analyzed as the sum of two terms:

$$C_2H_6.nH_2O_{(s)} \rightarrow \left(1 - \frac{nxC_2H_6}{1 - xC_2H_6}\right) C_2H_6\,_{(g)} + n\,H_2O_{(l,\ C2H6sat)} \quad (\Delta H_{1a}) \tag{9}$$

$$C_2H_6.nH_2O_{(s)} \rightarrow \left(\frac{nxC_2H_6}{1-xC_2H_6}\right) C_2H_{6\,(g)} + n\,H_2O_{(l)} \qquad (\Delta H_{1b})$$

(10)

The term H_2O (l, C_2H_6 sat) refers to a mole of liquid water which is saturated with respect to ethane at the given temperature and pressure. The Clapeyron equation will be used to find ΔH_{1a}, while solubility data will be used to find ΔH_{1b}. For ΔH_2, enthalpy can be determined directly because solubility of ethane in ice is negligible.

The Clapeyron equation is presented without derivation gives;

$$\Delta H = T\,\Delta V \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) \tag{11}$$

From there, the analysis begins with the determination of ΔH_2 because is it straightforward and the value of ΔH_2 will be used in order to find ΔH_1 and n.

The (p, T) of three phase equilibrium (ice, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Roberts *et al.* (1940)
- Falabella and Varpee (1974)
- Deaton and Frost (1946)

The (p, T) data will be plotted as ln (p/ MPa) vs. K/T graph. Then, the graph will be least-squares fitted to a fourth order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_2 will be calculated manually while; the d*p*/ d*T* will be calculated using the equilibrium graph plotted before. Based on the graph, the d*p*/ d*T* can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i(\frac{K}{T})^i$$

(12)

The function is differentiated with respect to 1/ *T* that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i(\frac{K}{T})^i$$

(13)

. Finally, d*p*/ d*T* at each temperature and pressure is found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2}\frac{\mathrm{d}\ln(p)}{\mathrm{d}(\frac{1}{T})}$$

(14)

The fit parameters of b_0, b_1, b_2 and b_3 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_2. ΔV_2 is equal to;

$n\ V_{ice}$ (volume of n moles ice) + V_{CO2} (volume of 1 mole ethane vapor) – V_{hyd} (volume of hydrate containing 1 mole ethane).

(15)

The parameters for each sections of volume can be obtained from the data collected by previous studies and NIST webbook. From there, the Clapeyron equation for ΔH_2 can be easily calculated once the value for ΔV_2 and dp/ dT has been determined for selected temperature and pressure.

The next step is to determine the ΔH_1, we starts with ΔH_{1a}.

The (p, T) of three phase equilibrium (liquid, hydrate, vapor) lines will be taken from experimental data collected by Sloan and Koh (2003). The data sets that will be used are shown below;

- Roberts *et al.* (1940)
- Galloway *et al.* (1970)
- Deaton and Frost (1946)
- Reamer *et al.* (1952)
- Holder and Grigoriou (1980)
- Holder and Hand (1982)

The (p, T) data will be plotted as ln (p/ MPa) vs. K/T graph. Then, the graph will be least-squares fitted to a third order polynomial with respect to the 1/T in order to get the same expression of parameters in the Clapeyron equation.

From the Clapeyron equation, the ΔV_{1a} will be calculated manually while; the dp/ dT will be calculated using the equilibrium graph plotted before. Based on the graph, the dp/ dT can be represented by the equation of;

$$\ln(p/MPa) = \sum_{i=0}^{i} b_i(\frac{K}{T})^i \tag{16}$$

The function is differentiated with respect to 1/ T that yield;

$$\frac{d\ln(p/MPa)}{d(K/T)} = \sum_{i=1}^{i} b_i (\frac{K}{T})^i$$

(17)

Finally, dp/ dT at each temperature and pressure is found by;

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(p)}{T^2}\frac{\mathrm{d}\ln(p)}{\mathrm{d}\,(\frac{1}{T})}$$

(18)

The fitted parameters of b_0, b_1, and b_2 can be obtained directly from the equation of the graph.

The next step is to calculate the ΔV_{1a}. ΔV_{1a} is equal to;

$\left(1 - \frac{nxC_2H_6}{1-xC_2H_6}\right)$ V_{CO2} (volume of n moles ice) + nV_{liq} (volume of 1 mole ethane vapor) – V_{hyd} (volume of hydrate containing 1 mole ethane).

(19)

The parameters for each sections of volume can be obtained from the data collected by previous studies. Each of the sections will be determined according to the function. From there, the Clapeyron equation for ΔH_{1a} can be easily calculated once the value for ΔV_{1a} and dp/ dT has been determined for selected temperature and pressure.

ΔH_{1b} can determined from the solubility data. The solubility can be evaluated by the available data using the Krichevsky-Kasarnorvsky (1935) equation;

$$\ln\left(\frac{f}{x_{C_2H_6}}\right) = \ln K_H + \frac{V\infty_{C_2H_6,H_2O}\,(p - p^s)}{RT}$$

(20)

Where f, fugacity of C_2H_6 in the gas phase; $x_{C_2H_6}$, mole fraction of C_2H_6 dissolved in the liquid phase; K_H, Henry's law constant; $V\infty_{C_2H_6,H_2O}$, partial molar volume of C_2H_6 in water at infinite dilution; p, total system pressure; p^s, vapor pressure of water at temperature T.

The partial molar volume, $V\infty_{C_2H_6,H_2O}$ at infinite dilution is independent of pressure and slightly dependent of temperature and can be determined by;

$$ln\ \left[V\infty_{C_2H_6,H_2O}/(\mathrm{m}^3.\mathrm{mol}^{-1}\right] = -10.275 + 1.23 \text{ x } 10^{-3}\left(\frac{\mathrm{T}}{K} - 273.15\right) \tag{21}$$

The ethane solubility is found from the measured value from Anderson (2004). Because of the mole fraction $x_{C_2H_6}$ is so low, the enthalpy of solution per mole of carbon dioxide can be equated with little error to the partial molar enthalpy of solution at infinite dilution which denoted by $\Delta H\infty_{C_2H_6,H_2O}$.

Based on Benson and Krause (1989), $\Delta H\infty_{C_2H_6,H_2O}$ can be known by equation;

$$\Delta H\infty_{C_2H_6,H_2O} = R\frac{d\ln K_H}{d(\frac{1}{T})} - T\frac{dV\infty_{C_2H_6,H_2O}}{dT}(p-p^s) + V\infty_{C_2H_6,H_2O}(p-p^s) + TV\infty_{C_2H_6,H_2O}\left(\frac{dp^s}{dT}\right) \tag{22}$$

The second term in equation is negligible since $V\infty_{C_2H_6,H_2O}$ is almost independent of T. also, the fourth term is negligible due to the smallness of the water vapor pressure at the temperatures of hydrate formation. Once calculated, the $\Delta H1_b$ can be determined just by simply multiply the expression of $\Delta H\infty_{C_2H_6,H_2O}$ with the $\left(-\frac{nxC_2H_{6,}}{1-xC_2H_{6,}}\right)$.

Finally, the enthalpy of dissociation of ethane hydrate ΔH_1 can be known by, the total submission of $\Delta H_{1a} + \Delta H_{1b}$. For the calculation of hydration number can only be done once the enthalpy of both reactions has been determined. The difference between enthalpy of both reactions will be divided with the enthalpy of fusion of water and the hydration number can be known.