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Determination of mixed hydrate thermodynamics for reservoir modeling

Nagasree Garapati
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Determination of Mixed Hydrate Thermodynamics for Reservoir Modeling

Nagasree Garapati

**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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Key words: Mixed Gas Hydrates, Thermodynamics, Phase Equilibrium, Structure Transitions, Empirical correlation, Cell Potential Code, Reference Parameters.

Abstract

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Nagasree Garapati

Natural gas hydrates are likely to contain more carbon than in all other fossil fuel reserves combined worldwide. Most of the natural gas hydrate deposits contain CH_4 along with other hydrocarbon gases like C_2H_6 , C_3H_8 and non-hydrocarbon gases like CO_2 and H_2S . Thus, if CH_4 stored in natural gas hydrates can be recovered, the hydrates would potentially become a clean energy resource for the next 10,000 years. The production of CH_4 from natural gas hydrate reservoirs has been predicted by reservoir simulators that implement phase equilibria data to predict various production scenarios. Therefore, it is very important to predict accurately phase equilibria of mixed hydrates. In this work an empirical correlation of dissociation pressure with respect to temperature and gas phase composition for CH_4 - C_2H_6 mixed hydrate system is developed by fitting to available experimental data. It is a simple method with limited accuracy. Statistical thermodynamics approach developed by van der Waals and Platteeuw in 1959 provides best approximation to predict the phase equilibrium data. They assumed that there are no lattice distortions due to the guest molecules, hence constant reference parameters are used for different guest molecules. Later, Hwang et al. by his molecular dynamics found that there are lattice distortions due to the guest molecules and Holder et al. proposed that the reference chemical potential difference $\Delta\mu_w^0$ and reference enthalpy difference Δh_w^0 varies with the guest molecule. In this work, a correlation of $\Delta\mu_w^0$ and Δh_w^0 with respect to guest molecular size is developed to estimate the values of $\Delta\mu_w^0$ and Δh_w^0 . The cell potential method developed by Anderson et al. is modified for variable reference parameters. The method is validated by reproducing the phase equilibria of simple hydrates and the structural transitions that are known to occur. Three-dimensional phase equilibria and structural transitions occurring in the mixed hydrates like CH_4 - C_2H_6 , CH_4 - N_2 and N_2 - CO_2 are predicted accurately without fitting to experimental data. The phase equilibria of CH_4 - CO_2 and CH_4 - N_2 - CO_2 hydrates are predicted to assess the production of CH_4 from the reservoirs by replacing CH_4 in the hydrate by pure CO_2 and N_2 + CO_2 mixture which serves dual purpose of CH_4 recovery and CO_2 sequestration.

Dedicated To My Grandfather

Ram Murthy Uppalapati

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1 Introduction

1.1 Definition

Clathrate hydrates, also known as gas hydrates, are nonstoichiometric crystalline inclusion compounds formed by the physically-stable interactions between water and relatively small guest molecules, where guest molecules are entrapped in the cavities built by water molecules. The most common guest molecules are methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide and hydrogen sulfide. The generic name “clathrate” is taken from a Greek word “khlatron” which means “bars”¹. Clathrates typically form under cold temperatures and relatively high pressures.

1.2 Overview and Historical Perspective

1.2.1 Discovery

Clathrate compounds were first observed in 1810 by Sir Humphrey Davy² while experimenting with chlorine and water mixtures, as the mixtures cooled, a solid material forming at temperatures above the normal freezing point of water was observed. The chlorine hydrate compositions were studied by Michael Faraday³ and suggested that its composition to be nearly 1 part of chlorine and 10 parts of water. In addition, there was some evidence that Joseph Priestley⁴ discovered SO₂ gas hydrate 30 years prior to Davy’s observation while performing cold experiments in his laboratory. Generally natural gas hydrates occurs, on land in permafrost regions, on the sea floor, in ocean sediments, and in deep lake sediments. Naturally-occurring gas hydrates were first discovered in association with cold subsurface sediments in the Siberian permafrost terrains in 1964⁵ and later in many marine sediments and in the Alaskan and

Canadian permafrost. Most commonly hydrates are known to form three different structures. Structure I hydrates are formed from gases that are provided by bacterial activity at shallow depths and contain 99% of methane and trace amounts of ethane and other non-hydrocarbon gases, while structure II and structure H are formed by gases produced by thermal pyrolysis of fossil organic matter which contains methane and significant amounts of other higher hydrocarbons (C₂-C₅)⁶. Therefore, the naturally occurring hydrates are mostly mixed hydrates of methane and other hydrocarbons like ethane, propane.

1.2.2 Hydrates in Industries

Between 1810 and 1900 most of the research on hydrates focused on finding the composition of the hydrates. After the discovery of pipeline plugging by hydrates at temperatures above the ice point by HammerSchmidt⁷ in mid-1930s, the focus of clathrate hydrates investigation evolved to include understanding the formation, dissociation conditions and phase equilibria.

Hydrates can be used for mass and energy storage. In 1942 M.E.Benesh⁸ proposed that hydrates can be used to store natural gas. Later, many investigations have been carried out in this area and investigations proved that storing natural gas in hydrates is technically feasible. However due to complexities in the process, the slow rate of hydrate formation, and the high cost of cooling it has not yet put in to common practice. They are useful in energy storage and recovery due to their heat of fusion and formation temperatures⁶, and are also used in sea water desalination⁹ and in light gases separation⁶.

1.2.3 Hydrates as a Possible Energy Source

More recently, natural gas hydrates have been considered as a large potential source of relatively clean energy. Hydrates are estimated to contain more carbon than in all other fossil fuel reserves combined worldwide. The breakdown of 1 volume of hydrate yields about 164 volumes of gas at 1 atm and 273 K¹⁰. The energy required for the dissociation of hydrate is less than 15% of the recovered energy. The estimations of hydrate occurrences in the world are based on assumptions made by each estimator. Gas hydrate estimates by different researchers are shown in Table 1.1. Trofimuk¹¹ was the first to estimate the extent of hydrate occurrences in 1973 with assumption that hydrates occur wherever suitable conditions of temperature and pressure exists. Worldwide, more than 90 hydrate occurrence sites have been identified, either directly or indirectly, as shown in Figure 1.1. Current estimates show that these hydrate sites could contain about 10^{15} to more than 10^{17} m³ of methane at standard temperature and pressure¹². The energy consumption of United States for 1000 years at current rate is around 10^{15} m³. Thus the resource of hydrates can become a potential clean energy source for up to 10,000 years¹³.

Figure 1.1. World Map of Natural Gas Hydrate Occurrence Sites.

Source: Lorenson, T. D.; Kvenvolden, K. A. "Global Occurrences of Gas Hydrate." *Geophysical Monograph*. 2001, 124, 3.

Table 1.1 Estimates of *In Situ* Methane Hydrate

Year	CH ₄ amount 10 ¹⁵ m ³ STP	Citations ^a
1973	3053.0	Trofimuk et al.
1977	1135.0	Trofimuk et al.
1982	1573.0	Cherskiy et al.
1981	120.0	Trofimuk et al.
1981	301.0	McIver
1974/1981	15.0	Makogon
1982	15.0	Trofimuk et al.
1988	40.0	Kvenvolden and Claypool
1988	20.0	Kvenvolden
1990	20.0	MacDonald
1994	26.4	Gornitz and Fung
1995	45.4	Harvey and Huang
1995	1.0	Ginsburg and Soloviev
1996	6.8	Holbrook et al.
1997	15.0	Makogon
2002	0.2	Soloviev
2004	2.5	Milkov
2005	120.0	Klauda and Sandler

^aRef 11, 14-30.

1.2.4 Carbon Dioxide Sequestration

Natural gas hydrates could be a source for sequestering carbon dioxide. The hydrate formation - dissociation conditions of CH₄ and CO₂ are different and the equilibrium pressures for CO₂ hydrate are lower when compared to that of CH₄ hydrate at temperatures below 285 K as shown in Figure 1.2. Therefore, it is thermodynamically possible to replace CH₄ in the natural gas hydrate with CO₂. In 1996 Ohgaki et al.³¹ was first to develop the idea of swapping CH₄ by CO₂ in gas hydrates. As CO₂ replaces CH₄ from the CH₄ hydrate it forms a mixed hydrate of CH₄-CO₂ as it cannot recover all the CH₄ present in the hydrate.

Figure 1.2 Thermodynamic Phase Diagrams for CH₄ and CO₂ Hydrates. Q₁: Lower Quadruple point Q₂: Upper Quadruple Point.

Therefore, accurate thermodynamic predictions of phase equilibria of mixed hydrates should prove to be a key tool in understanding the production and replacement of CH₄ from the natural gas hydrates.

1.3 Clathrate Hydrate Structures

There are structure transitions that are known to occur with temperature in simple hydrates and with gas phase composition in mixed hydrates. During the production of CH₄ from the natural gas hydrate reservoirs as the CH₄ gas is evolved, the hydrate will be enriched in C₂H₆ and there may be a structural change in the hydrate due to the presence of C₂H₆. In order to understand these structure transitions it is important to have the knowledge about the geometry of the gas hydrate structures.

In 1948 Powell³² at the University of Oxford was the first to describe the structure of clathrate and labeled them “clathrates”. Generally, upon freezing water forms ice in a hexagonal crystal structure. Though gas hydrates mostly contains water, they can form into cubic lattice structure which entraps the guest molecules. Three common crystal structures are formed by gas hydrates, two cubic structures – structure I and structure II and a hexagonal structure – structure H.

Structure I gas hydrates consists of 46 water molecules per unit cell arranged in two 12-sided cages (5^{12} , pentagonal dodecahedra) and six 14-sided cages ($5^{12} 6^2$, tetrakaidecahedra), and can be occupied by at most 8 guest molecules of diameters between 4.2 Å and 6 Å like methane, ethane, carbon dioxide and hydrogen sulfide. There has been evidence of multiple small gas molecules such as H₂ occupying same cage. The cavities of structure I are shown in Figure 1.3. It forms a primitive cubic lattice with lattice constant of 12.0 Å. The hydrate lattice structure is shown in Figure 1.4. The ideal, fully-occupied guest/water ratio is 8G·46H₂O or G·5.75H₂O where G is the guest molecule⁶. However, the fraction of the cages that are occupied varies according to temperature and pressure. This will be discussed further in section 2.2.3.

Structure II gas hydrates consists of 136 water molecules per unit cell arranged in sixteen 12-sided cages (5^{12} , pentagonal dodecahedra) and eight 16-sided cages ($5^{12} 6^4$ hexakaidecahedra), and can be occupied by at most 24 guest molecules of diameters less than 4.2 Å like nitrogen and hydrogen and molecules of diameters between 6 Å and 7 Å like propane and iso-butane. The cavities of the structure II are shown in Figure 1.5. It forms a face center cubic lattice with a lattice constant of 17.3 Å. The lattice structure is shown in Figure 1.6. The ideal, fully-occupied guest/water ratio is 24G·136H₂O or G·5.67H₂O where G is the guest molecule⁶.

Structure H gas hydrates was first reported by Ripmeester et al.³³ It consists of 34 water molecules per unit cell arranged in 3 (5^{12} pentagonal dodecahedral cages), 2 ($4^3 5^6 6^3$ irregular dodecahedral cages) and 1 ($5^{12} 6^8$ icosahedral cages). Larger molecules of diameter between 7 Å and 9 Å like iso-pentane and neohexane can form structure H along with small molecules like methane, hydrogen sulfide or nitrogen. The cavities of structure H are shown in Figure 1.7 and the lattice structure in Figure 1.8. Simple hydrates of S H are not formed at normal temperature hence the concept of ideal guest/water ratio is only applicable for two/more guests⁶.

The structure of the hydrate changes significantly in presence of other guest molecules, like structure I CH_4 hydrate changes to structure II by addition of trace amounts of C_2H_6 and similarly structure II N_2 hydrate changes to structure I by trace amounts of CO_2 . This structural change will result in significant change in hydration number and therefore the hydrate concentration. The phase equilibrium calculations vary with structure as discussed in section 2.2.3. The properties of the structures are tabulated in Table 1.2⁶.

Table 1.2 Geometry of Cages

Hydrate Crystal Structure Cavity	Structure I		Structure II		Structure H		
	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12} 6^2$	5^{12}	$5^{12} 6^4$	5^{12}	$4^3 5^{12} 6^3$	$5^{12} 6^8$
No. of cavities/unit cell	2	6	16	8	3	2	1
Average cavity radius	3.95	4.33	3.91	4.73	3.94	4.04	5.79
Variation in radius (%)	3.4	14.4	5.5	1.73	4.0	8.5	15.1
No. of water molecules / cavity	20	24	20	28	20	20	36

Source: Sloan, E. D.; Koh, C. A. *Clathrate hydrates of natural gases*, 3rd Ed, 2007.

Figure 1.3 Structure I Cavities (a) Small Cage (5^{12} , Pentagonal dodecahedron) (b) Large Cage ($5^{12} 6^2$, Tetrakaidecahedron)

Figure 1.4 Structure I Hydrate Lattice Structure

Figure 1.5 Structure II Cavities (a) Small Cage (5^{12} , Pentagonal dodecahedron) (b) Large Cage ($5^{12} 6^4$, Hexakaidecahedron)

Figure 1.6 Structure II Hydrate Lattice Structure

Figure 1.7 Structure H Cavities (a) Small Cage (5^{12} , Pentagonal dodecahedron) (b) Medium Cage ($4^3 5^6 6^3$, Irregular dodecahedron) (c) Large cage ($5^{12} 6^8$, Icosahedron)

Figure 1.8 Structure H Hydrate Lattice Structure.

1.4 Hydrate Stability

The necessary conditions for hydrate formation and stability are driven by the thermodynamics of the system and can be summarized by:

1. Low Temperatures
2. High Pressures
3. Adequate amount of water molecules
4. Adequate amount of gas molecules.

The gas hydrate stability zone (GHSZ) is the range of depths of subsea or subsurface at which natural gas hydrates can form and remain stable at existing temperature, pressure and local gas composition⁵.

For marine environments, the GHSZ begins at a depth below 300-600 m of water and extends hundreds of meters below the seafloor with a temperature ranging from 2°C to 20°C³⁴.

For permafrost environments, the GHSZ begins at a depth of 100-300 m and extends hundreds of meters into the subsurface based on base of permafrost with a temperature ranging from -10°C to 20°C³⁴.

The conditions for methane gas hydrate formation are illustrated in Figure 1.9 for both permafrost and sea floor regions, pressure and depth are shown on the vertical axis and temperature is shown on the horizontal axis. The depth of hydrate stability zone shifts due to geothermal gradient. Methane hydrate, being less dense than water, would float upward if released and would dissociate due to lower pressure or higher temperatures.

Figure 1.9 Methane Hydrate Stability Zones (a) Permafrost Regions and (b) Sea Floor Regions.

The stable regimes are governed by the hydrate thermodynamic phase equilibria. The phase boundary moves to the left in the presence of salt in the water and it moves to right in presence of other gases like carbon dioxide, hydrogen sulfide and other hydrocarbons i.e., the methane hydrate becomes unstable in the presence of salts hence they can be used as inhibitors and in the presence of other hydrocarbons like ethane the hydrate becomes more stable at relatively low pressure. In this work phase boundaries of various mixed hydrates are calculated, hence the changes to GHSZ in presence of other hydrocarbons and non hydrocarbon gases.

1.5 Production of Gas from Hydrates

Since the Worldwide resource potential of gas hydrate as an energy source is substantial, it is important to understand and study different techniques that may be used for recover the methane trapped in gas hydrates. Different techniques proposed for production of methane from gas hydrates include depressurization, thermal stimulation, inhibitor injection and gas exchange.

1.5.1 Depressurization

The objective of this method is to decrease the pressure within the hydrate stability zone, causing the hydrate to decompose and releasing the methane that will migrate towards the wellbore. This method is thought to be the most economically viable because there is no extra heat introduced into the system⁵.

1.5.2 Thermal Stimulation

The temperature of hydrate stability zone may be increased by a source of heat provided either directly by injecting steam, hot water, or any other heated liquid or indirectly by electric or sonic means, causing the hydrate to decompose. The thermal stimulation method is likely to be expensive because a large fraction of the heat supplied is lost to heat the porous media in which the hydrate is formed⁵.

1.5.3 Inhibitor Injection

Chemical inhibitor such as salts, alcohols and glycols could be used to shift the pressure-temperature equilibrium conditions leading to dissociation of the gas hydrate. This method is

also likely to be expensive due to the cost of the chemicals. Additionally it would require high permeability in the hydrate-bearing sediment in order to allow for fluid injection⁵.

1.5.4 Gas Exchange by CO₂ and CO₂+N₂

Each of the three processes discussed previously may cause geomechanical stress on the reservoir leading to subsidence. The proposed method of recovery of CH₄ by replacement of CH₄ with CO₂ through injection of pressurized CO₂ would result in a greatly decreased perturbation to the solid hydrate. This process could be advantageous because of the potential for sequestering CO₂ along with CH₄ recovery. CO₂ hydrate is thermodynamically more stable than CH₄ hydrate at temperatures below 283 K due to the lower equilibrium pressures of CO₂ hydrate compared to that of CH₄ hydrate. The Gibb's free energy for the replacement is negative indicating the process is thermodynamically feasible³⁵. It may also enable the sea floor to maintain its structural integrity even after the recovery of CH₄ because CO₂ also forms structure I hydrate similar to CH₄ hydrate. Hence the hydrate maintains same crystalline structure even after replacement. The recovery rate of CH₄ could be increased by using a binary mixture of N₂ and CO₂, because N₂ expels CH₄ from the small cages and CO₂ from the large cages of structure I. CO₂ does not occupy the small cage while N₂, because of its small size, readily occupies small cage. Hence N₂ acts as an enhancing factor in recovery of CH₄. Additionally the direct use of N₂+CO₂ removes the requirement of CO₂ purification before the replacement process³⁶.

All the production methods involve the change in the phase equilibrium conditions of the gas hydrates and are illustrated in Figure 1.10. The data for CH₄ and CO₂ phase equilibrium is obtained by predictions of cell potential code developed by Anderson et al.³⁷ and the data of phase equilibrium of CH₄ hydrate in presence of inhibitors is obtained from experimental data of

Ng and Robinson³⁸. Therefore it is necessary to accurately predict the phase equilibrium conditions, and the structure of methane mixed hydrates to assess the production of CH₄ from the natural hydrates.

Figure 1.10 Phase Equilibrium Diagram of CH₄ Hydrate with Different Production Methods.

1.6 Reservoir Simulators

The field scale experiments and the equipment required for the production are very expensive. Reservoir simulators can be used to predict production potentials of hydrate wells and to determine which technique best suits for that hydrate reservoir. In reservoir simulations, computer models are used to predict the flow of fluids (like oil, water and gas) through porous media over time. Reservoir simulation models are mainly used by oil and gas companies in developing new fields also in developed fields to predict the production rates which are needed in making investment decisions. They are also used in prediction of gas from the hydrate reservoirs.

Reservoir simulators involve solutions for highly complex combinations of fluid, heat and mass transport equations and formation/dissociation of multiple solid phases. The physical and chemical properties of the reservoir depend on the amount of hydrate present in the system at any time. Different models and mathematical algorithms have been used to solve these problems, with each approach having certain advantages and disadvantages. Different reservoir simulators used to study gas hydrate reservoirs are:

1. CMG STARS³⁹
2. HydrateResSim⁴⁰
3. MH-21 HYDRES⁴¹
4. STOMP-HYD⁴²
5. TOUGH+HYDRATE⁴³.

In the prediction of CH₄ production from hydrate reservoirs, the pressure and temperature of the I-H-V and L_w-H-V three-phase lines are of particular interest as they describe the limits of hydrate formation and dissociation conditions. For pure CH₄ hydrate, the above reservoir simulators except for STOMP-HYD uses regression expressions developed by Kamath⁴⁴ and Moridis⁴⁵ to obtain equilibrium pressure and temperature relationships. These regression equations cannot predict the occupancies and composition of the hydrates and can be used only for pure hydrates. But, natural gas hydrates are not pure gas hydrates, as they contain trace amounts of other hydrocarbons and non hydrocarbon gases along with methane. The CH₄ trapped in hydrate reservoirs can be recovered by injection of pure CO₂ and CO₂+N₂ after replacing CH₄ from the natural gas hydrate they form mixed hydrate of CH₄-CO₂ and CH₄-CO₂-N₂ respectively. Hence a computationally tractable method has to be developed to implement

into the existing reservoir models for mixed hydrates which can also predict other hydrate properties.

1.7 Estimation Techniques for Phase Equilibria

In the past different predictions techniques have been used to calculate the three-phase (L_w -H-V) equilibrium conditions of gas hydrates:

1. Gas gravity method
2. K_{vsi} Method
3. Statistical Thermodynamics approach.

The first two methods are hand calculation methods, both involve the use of charts. The drawback for these methods is that they are not accurate. The third method is based upon statistical thermodynamics which provides the best approximation to predict the phase equilibrium data of gas hydrates but this method involves a number of iterations steps⁶. The techniques are discussed in detail in chapter 2. Therefore, in this work, we will develop methods that are faster and more accurate for use in reservoir simulators.

1.8 Motivation

The accurate predictions of hydrate-forming conditions and phase equilibrium data are necessary for production of CH_4 gas from the natural gas hydrates. Naturally-occurring hydrate reservoirs mostly contain methane along with other hydrocarbon and non-hydrocarbon gases. The ability to predict mixed hydrates behavior is necessary in order to assess the production ability of these reservoirs. The phase equilibrium conditions of a pure hydrate changes significantly and the structure of the hydrate formed may also change due to the presence of other hydrocarbons. Any

structural change could result a significant change in the hydration number and hence the concentration of hydrocarbon in the hydrate. Both methane and ethane form structure I as simple or single-component hydrates but the mixture undergoes a transition from structure I to structure II at a methane mole fraction of 0.72 and 0.75 at 274.2 K⁴⁶⁻⁴⁷. Nitrogen forms structure II as a simple hydrate but with methane and carbon dioxide it forms structure I. Nitrogen-carbon dioxide hydrate forms structure II when the carbon dioxide composition is above 0.01 mole fraction in the gas mixture⁴⁸. The methane-nitrogen mixed hydrate undergoes a transition in its structure at a mole fraction of 0.252 and 0.285 of methane⁴⁹. The structure of the mixed gas hydrate depends on the relative gas composition. Because, the current state-of-art in the reservoir simulations only accounts for single-guest hydrates, we will develop a method to incorporate multiple guest hydrates.

There are very few measurements of the hydrate phase compositions, due to experimental difficulty, which arises due to large amount of free water present often gets occluded in hydrate mass and separation of hydrate and water is difficult, hence the calculation of hydrate occupancy is often inaccurate. Therefore there is a need to develop a method which can predict phase equilibria curve along with the hydrate phase composition.

Methods for production of methane gas from the hydrates include thermal recovery, depressurization and injection of chemical inhibitors. All the techniques involve perturbations to the phase equilibrium curve⁵. During the production from reservoirs as the methane gas is evolved the hydrate will be enriched with the other gases present like ethane, and it becomes more stable and favorable for formation of secondary hydrate. Therefore, it is important to know the effects of the small amounts of the other gases present in the hydrate on production and hydrate reforming in a reservoir.

A newly proposed method for the production of CH_4 gas is the use of CO_2 gas. CH_4 gas from the hydrates would be replaced by CO_2 gas forming CO_2 hydrate. This will serve the dual purpose of sequestering CO_2 gas, a global warming gas, and the recovery of methane gas which can be used as a fuel³¹. Both CH_4 and CO_2 forms structure I hydrate hence it enables the seafloor to remain stable even after the replacement process. It has been found experimentally that the rate of recovery of methane from the hydrate using carbon dioxide is around 64%⁵⁰. However, it is necessary to predict the phase equilibria of the CH_4 - CO_2 mixed hydrate in reservoir simulators to provide for the evaluation of the scale up of the process.

The fraction of methane recovered from the hydrate can be improved to 85% by using N_2 - CO_2 gas mixture instead of pure CO_2 . CH_4 from large cages is mostly swapped by CO_2 while that from the small cages by N_2 . Direct use of mixture reduces the effort of purification of CO_2 . To understand the process of swapping the ternary system CH_4 - N_2 - CO_2 has to be studied³⁶.

As CH_4 from the hydrate reservoirs can become a potential energy resource. The production of CH_4 from the hydrate reservoirs has become significant, it is not economic to conduct the field scale experiments as the equipment and the experiments are expensive. The reservoir simulators are used to model the production scenario that uses phase equilibria data of the hydrates to predict the production rates. Currently reservoir simulators are modeled only for the simple hydrates but production of CH_4 from the hydrate reservoirs involves mixed hydrates like CH_4 - C_2H_6 , CH_4 - CO_2 etc. The phase equilibria data for the mixtures are limited, therefore predictive methods like correlations and cell potential predictions are developed in this work and these predictions can be implemented into the simulators to predict the reservoir responses.

1.9 Thesis Objectives

The overall goal of this thesis is to understand the phase equilibria of the simple and mixed hydrates and to develop method of implementing phase equilibria prediction into reservoir models. The equilibrium curve of the mixed hydrate and structural transitions are predicted using cell potential model. Specific objectives of this thesis are:

- To develop an empirical correlation of dissociation pressure with respect to temperature and gas phase composition of the mixed hydrates like methane-ethane hydrate system.
- To modify the cell potential method for variable reference parameters and validate the model by predicting phase equilibrium data of simple hydrates.
- To determine the three- dimensional (P - T - x) phase diagram and structural transitions for the methane-ethane mixed hydrate.
- To predict methane and carbon dioxide mixed hydrate phase equilibrium so as to understand the swapping of CH_4 by CO_2 for production of CH_4 gas from the gas hydrate and sequestration of CO_2 .
- To calculate the phase equilibrium conditions for methane-nitrogen and nitrogen-carbon dioxide mixed hydrates. Nitrogen forms structure II as a simple hydrate but along with other guests it can form structure I.
- To evaluate the methane, nitrogen and carbon dioxide ternary system. The recovery of methane from the gas hydrates using CO_2 can be improved by using N_2 and CO_2 mixture. Nitrogen mostly occupies small cages in the hydrate structure while carbon dioxide occupies large cages. N_2 could act as an enhancing agent for the production of methane gas from the hydrate.

1.10 References

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2 Hydrate Phase Equilibria Predictions

In this chapter the theoretical framework for the calculation of gas hydrate phase equilibria is discussed. The various techniques used for predicting the gas equilibria and the method employed in this work are discussed. The conditions of three-phase (L_w -H-V) equilibrium are most useful in predicting the production rates of CH_4 from natural gas hydrates as the production of CH_4 gas from the hydrate reservoir is governed by the gas hydrate phase equilibrium. Along with temperature and pressure conditions it is also important to have knowledge about the other hydrate properties like cage occupancies and hydrate phase compositions. Methods have been developed since the 1940's to predict the phase equilibria of gas hydrate systems. Initially hand calculation methods were developed which are inaccurate and are unable to calculate all of the hydrate properties, since 1959, statistical thermodynamic approaches have been developed that provide the best prediction of hydrate phase equilibrium data.

Three common techniques used to calculate the three-phase (L_w -H-V) equilibrium conditions are:

1. Gas gravity method
2. K_{vs} Method
3. Statistical Thermodynamics approach

2.1 Gas Gravity Method

The gas gravity method is a simple method for estimating the hydrate formation conditions using the Katz gas gravity charts¹, where gas gravity is defined as the ratio of the molecular mass of the hydrate-forming gas to that of air. The original charts were generated for hydrates containing only hydrocarbons, hence they should be used with care for hydrates that contain considerable

amount of other gases like CO₂, H₂S and N₂. Though the method is simple it is not very accurate and hydrate composition cannot be calculated using the gas gravity method². In approximately 60 years of its origin, there are more hydrate data and prediction methods are developed that caused the gravity method to be used as a first estimate. Therefore more recent methods are discussed in this work.

2.2 K_{vsi} Method

The Distribution Coefficient (K_{vsi} -value) Method was developed by Wilcox et al.³ and confirmed by Carson and Katz⁴. Carson and Katz observed that the hydrate composition varies with the temperature and pressure and therefore defined a vapor-solid distribution coefficient (K_{vsi}) for each component.

$$K_{vsi} \equiv y_i / x_{si} \quad (2.1)$$

where y_i = mole fraction of component i in the water-free vapor and

x_{si} = mole fraction of component i in the water-free solid hydrate.

The distribution coefficient (K_{vsi}), a function of temperature and pressure is either calculated from the charts where the K_{vsi} values are presented as function of temperature and pressure or from the equation obtained by fitting all the K_{vsi} values from the chart

$$\begin{aligned} \ln K_{vsi} = & A + B * T + C * P + D * T^{-1} + E * P^{-1} + F * P * T + G * T^2 + H * P^2 + I * P \\ & * T^{-1} + J * \ln(P * T^{-1}) + K * (P^{-2}) + L * T * P^{-1} + M * T^2 * P^{-1} + N * P \\ & * T^{-2} + O * T * P^{-3} + Q * T^3 + R * P^3 * T^{-2} + S * T^4 \end{aligned} \quad (2.2)$$

The K_{vsi} -value charts or equation are then used to estimate the hydrate forming conditions. The technique used in the calculation of the equilibrium conditions involves the calculation of K_{vsi} value such that the sum of mole fraction of each component in the vapor phase divided by the K_{vsi} value equals unity at the three- phase equilibrium conditions.

$$\sum_{i=1}^n \frac{y_i}{K_{vsi}} = 1.0 \quad (2.3)$$

Two pressures, P_1 and P_2 are assumed at a given temperature and gas composition such that for one K_{vsi} (P_1) value the ratio is greater than unity and for the other K_{vsi} (P_2) value the ratio is less than unity. The equilibrium pressure is interpolated between these two values such that the ratio is equal to unity. A similar technique is used for calculating the equilibrium temperature at a given pressure and gas composition. The K_{vsi} charts for methane are obtained from the experimental data points and the K_{vsi} charts for guests other than methane are derived from the binary experimental phase equilibrium data, based on the K_{vsi} value of methane. At an experimental hydrate formation temperature, pressure and gas composition, the values of y_i are fixed and the K_{vsi} value of methane is read from the chart. Therefore, the only unknown is the K_{vsi} value of second component which calculated by satisfying the Equation 2.3. The accuracy of the K_{vsi} values for other components depends on the accuracy of the methane charts since they are derived from the methane charts, hence have to be used with caution for mixtures containing considerable amount of heavy and non combustible gases. The K_{vsi} value charts are obtained in certain temperature range above ice point (273-290 K). The method considers both the gas phase and hydrate phase as an ideal solution where the K_{vsi} value of a given component is independent of other components present in the solution, i.e.; there are no interaction between molecules. This assumption is acceptable for hydrocarbons but it cannot be applicable for dense gas phases. The

method was developed preceded the knowledge of hydrate structures, it is impossible for one set of K_{vsi} values to serve for both hydrate structures.

The phase equilibrium data of $\text{CH}_4\text{-C}_2\text{H}_6$ mixed hydrate is calculated using this method. At a given temperature for each gas composition the initial guess should be different. Though the calculations are simple, it predicted the phase equilibria with an average absolute deviation of 31% in the temperature range of 273-283 K. Therefore, there is a need to develop a more accurate method which can be used for both structures.

2.3 Statistical Thermodynamics Approach

The pressure and temperature conditions for the formation or dissociation of a hydrate are governed by the equilibrium thermodynamics. According to standard thermodynamic phase equilibrium criteria, the chemical potential of each component must be the same in every phase. Thus, the phase equilibrium for gas hydrates can be defined as:

$$\mu_w^H(T, P) = \mu_w^{L,\alpha}(T, P) \quad (2.4)$$

$$\mu_w^\beta(T, P) - \mu_w^H(T, P) = \mu_w^\beta(T, P) - \mu_w^{L,\alpha}(T, P)$$

$$\Delta\mu_w^{\beta-H}(T, P) = \Delta\mu_w^{\beta-L,\alpha}(T, P) \quad (2.5)$$

where $\mu_w^H(T, P)$ = chemical potential of water in hydrate phase, H

$\mu_w^{L,\alpha}(T, P)$ = chemical potential of water in liquid aqueous phase, L or ice phase, α depending on whether the temperature, T is above or below 273.15 K, the freezing point of water.

and $\mu_w^\beta(T, P)$ = chemical potential of water in hypothetical empty hydrate lattice, β .

2.3.1 van der Waals and Platteeuw Method

The first statistical thermodynamic approach to predict phase equilibrium conditions was developed by Barrer and Stuart⁵. A much more successful method was later developed by van der Waals and Platteeuw⁶ based on classical Langmuir-type adsorption theory with these five basic assumptions:

1. The guest molecules do not distort the cavity.
2. Each cavity can contain at most one guest molecule.
3. There are no interactions between the guest molecules.
4. The internal partition functions for guest molecules are equal to that of the free guest molecules.
5. Classical statistics are valid.

The chemical potential difference between water in empty hydrate lattice and water in hydrate phase can be expressed as:

$$\Delta\mu_w^{\beta-H}(T, P) = kT \sum_i v_i \ln (1 + \sum_J C_{Ji} f_J) \quad (2.6)$$

where v_i = no. of type i cavities per water molecule, k = Boltzmann's Constant, f_J = fugacity of guest component J calculated by Peng- Robinson equation of state⁷, and C_{Ji} = Langmuir constant given by $C_{Ji} = \frac{Z_{Ji}}{kT}$ where Z_{Ji} is the configurational integral, Z_{Ji} is determined by the volumetric interaction of the potential energy between the guest and host molecules.

$$C_{ij} = \frac{1}{kT} \int \exp\left(\frac{-W(r, \theta, \phi)}{kT}\right) dV \quad (2.7)$$

where W = potential function describing the guest-water interactions in the hydrate phase.

van der Waals and Platteeuw used the Lennard-Jones-Devonshire⁸ (LJD) theory to calculate interactions between the guest molecule and surrounding water molecules. This model assumes that $W(r)$ is a suitable average of $W(r, \theta, \phi)$ without actually averaging it. The smoothed cell Langmuir constant is given as:

$$C_{ij}^* = \frac{4\pi}{kT} \int_0^R \exp\left(\frac{-W_1(r)}{kT}\right) r^2 dr \quad (2.8)$$

A Lennard-Jones 6-12 pair potential was used to calculate the binary interaction between guest and water molecules. The model works well for monoatomic or spherical molecules.

McKoy and Sinanoglu⁹ proposed to use Kihara potential instead of Lennard-Jones potentials for rod-like molecules. Parrish and Prausnitz¹⁰ improved the van der Waals and Platteeuw⁶ model with Kihara potentials for multicomponent gas hydrates. They reported Kihara parameters for different guest components by fitting the experimental data and proposed empty hydrate lattice thermodynamic properties. These properties have been used by other researchers since empty hydrate is not thermodynamically stable and its properties cannot be measured. They also provided an algorithm for calculating the phase equilibrium conditions of gas hydrates. The model is accurate within the temperature range of fit. The inaccuracy of model is mainly due to the assumptions that the water molecules are spread over a sphere of radius R and only first shell of water molecules are considered for total guest-host interactions. Many researchers have proposed and successfully implemented improvements to these early assumptions.

2.3.2 Hydrate Thermodynamics

For structure I there are 2 small cavities, 6 large cavities and 46 water molecules, therefore the expression for the chemical potential of the structure I hydrate can be expressed as

$$\frac{\Delta\mu_w^{\beta-H}(T,P)}{kT} = \frac{1}{23}\ln(1 + \sum_J C_{J1} f_J) + \frac{3}{23}\ln(1 + \sum_J C_{J2} f_J) \quad (2.9)$$

For structure II there are 16 small cavities, 8 large cavities and 136 water molecules, hence the corresponding expression is

$$\frac{\Delta\mu_w^{\beta-H}(T,P)}{kT} = \frac{2}{17}\ln(1 + \sum_J C_{J1} f_J) + \frac{1}{17}\ln(1 + \sum_J C_{J2} f_J) \quad (2.10)$$

Clathrates are non-stoichiometric compounds, therefore all the cavities need not be filled by a guest component. The probability of finding the guest component, J in the cavity of type i is known as cage occupancy, $y_{ji} \leq 1.0$ which depends on equilibrium conditions. Mathematically, the cage occupancy y_{ji} follows Langmuir adsorption isotherm and is related to Langmuir constant as:

$$y_{ji} = \frac{C_{ji}f_j}{1 + \sum_J C_{ji}f_j} \quad (2.11)$$

Therefore, the chemical potential difference between water in empty hydrate lattice and water in hydrate phase in terms of cage occupancy can be given as

$$\Delta\mu_w^{\beta-H}(T, P) = -kT \sum_i v_i \ln(1 - \sum_J y_{ji}) \quad (2.12)$$

Holder et al.¹¹ proposed an equation for the chemical potential difference between water in empty hydrate lattice and water in liquid aqueous phase or ice phase as:

$$\frac{\Delta\mu_w^{\beta-L,\alpha}(T,P)}{kT} = \frac{\Delta\mu_w^{\beta-L,\alpha}(T_0,0)}{kT} - \int_{T_0}^T \left[\frac{\Delta h_w^{\beta-L,\alpha}(T)}{kT^2} \right]_P dT + \int_0^P \left[\frac{\Delta V_w^{\beta-L,\alpha}}{kT} \right]_T dP - \ln a_w^L \quad (2.13)$$

where $\Delta\mu_w^{\beta-L,\alpha}(T_0, 0)$ is the reference chemical potential difference between water in empty hydrate lattice and water in liquid aqueous phase or ice phase at reference temperature, T_0 , and zero pressure. The temperature dependence of enthalpy difference is given as:

$$\Delta h_w^{\beta-L,\alpha}(T) = \Delta h_w^{\beta-L,\alpha}(T_0) + \int_{T_0}^T \Delta C_P^{\beta-L,\alpha}(T) dT \quad (2.14)$$

where $\Delta h_w^{\beta-L,\alpha}(T_0)$ is the reference enthalpy difference between water in empty hydrate lattice and water in liquid aqueous phase or ice phase at reference temperature, T_0 , and the heat capacity difference between the empty hydrate lattice and the water phase is approximated as:

$$\Delta C_P^{\beta-L,\alpha}(T) = \Delta C_P^{\beta-L,\alpha}(T_0) + b^{\beta-L,\alpha}(T - T_0) \quad (2.15)$$

where $\Delta C_P^{\beta-L,\alpha}(T_0)$ is the reference heat capacity difference and the constant $b^{\beta-L,\alpha}$ represents the temperature dependence of heat capacity. The volume difference $\Delta V_w^{\beta-L,\alpha}$ is assumed to be constant and the last term in the Equation (2.13) involving the activity coefficient of water, a_w^L is given as:

$$a_w^L = \frac{f_w^L}{f_w} \quad (2.16)$$

where f_w^L is fugacity of water in the water-rich aqueous phase and f_w is fugacity of pure water. The activity coefficient of water is taken to be one for slightly soluble gases like hydrocarbons and for soluble gases like carbon dioxide it is calculated using Henry's Law.

2.3.3 Thermodynamic Reference Parameters

The reference chemical potential difference, $\Delta\mu_w^{\beta-L,\alpha}(T_0, 0)$ and the enthalpy difference, $\Delta h_w^{\beta-L,\alpha}(T_0)$ was assumed to be constant for any guest molecules in van der Waals Platteeuw⁶ model due to assumption that guest molecules do not affect the host-host interactions. The reference parameters obtained from the literature are tabulated in Table 2.1.

Table 2.1 Thermodynamic Reference Parameters for Structure I and Structure II Hydrate from Literature.

Structure I (J/mol)		Structure II (J/mol)		Source ^a
$\Delta\mu_w^{\beta-L,\alpha}(T_0, 0)$	$\Delta h_w^{\beta-L,\alpha}(T_0)$	$\Delta\mu_w^{\beta-L,\alpha}(T_0, 0)$	$\Delta h_w^{\beta-L,\alpha}(T_0)$	
699	0	820	0	van der Waals and Platteeuw (1959) Barrer and Ruzicka (1962) Sortland and Robinson (1964) Child (1964) Parrish and Prausnitz (1972) Holder (1976) Dharmawardhana, Parrish and Sloan (1980) Holder, Malekar, and Sloan (1984) John, Papadopoulos, and Holder (1985) Davidson, Handa, and Ripmeester (1986) Handa and Tse (1986) Cao, Tester, and Trout (2002) Anderson, Tester, and Trout (2004)
		366-537		
		833		
1255.2	753	795	837	
1264	1150		808	
1155	381		0	
1297	1389	937	1025	
1299	1861			
1120	931	1714	1400	
1297				
1287	931	1068	764	
1236	1703			
1203	1170	1077	1294	

^aRef 6,15-26

Later, Hwang et al.¹², by molecular dynamic simulations on the unit cell of the gas hydrates with different guest molecules, proposed that guest molecules can have an impact on the host-host interactions in the lattice thus violating assumption 1. Zele et al.¹³ developed an empirical correlation between reference chemical potential and the cavity radius.

$$R = A + B \times \Delta\mu_w^0 \quad (2.17)$$

where R is the radius in Å and $\Delta\mu_w^0$ is in cal/mol. A and B are constants for three water shells for each type of cavity. Lee and Holder¹⁴ developed correlations for $\Delta\mu_w^0$ as a function of the Kihara hard-core parameter a , for structure I and structure II:

$$\left. \begin{array}{l} \text{for Structure I } \Delta\mu_w^0 = 133.39 \exp(0.0213 \times a), \quad R^2 = 0.9058 \\ \text{for Structure II } \Delta\mu_w^0 = 171.91 \exp(0.0101 \times a), \quad R^2 = 0.8810 \end{array} \right\} \quad (2.18)$$

where a is the Kihara parameter in pm and $\Delta\mu_w^0$ is in cal/mol. The reference chemical potential, $\Delta\mu_w^{\beta-L,\alpha}(T_0, 0)$ and enthalpy difference $\Delta h_w^{\beta-L,\alpha}(T_0, 0)$ depend on the guest molecule, hence it is important to develop a correlation between the reference parameters and the guest molecule. In this work, the reference chemical potential and enthalpy differences are considered to be function of the diameter of the guest and a correlation between the reference chemical potential, enthalpy difference and the diameter is obtained and used in the model to obtain variable reference parameters. The values of other reference parameters used in this work are tabulated in Table 2.2.

Table 2.2 Thermodynamic Reference Properties for Structure I and Structure II Hydrates; $T_0=273.15$ K

	Structure I	Structure II	Source
$\Delta V_w^{\beta-\alpha}(\text{m}^3/\text{mol})^a$	3.0 E-6	3.4 E-6	27
$\Delta V_w^{L-\alpha}(\text{m}^3/\text{mol})$	-1.598E-6		
$\Delta h_w^{L-\alpha}(T_0)$ (J/mol)	6009.5		
$\Delta C_p^{\beta-L}(T_0)$ (J/mol·K)	$-37.32+0.179(T - T_0)$		11
$\Delta C_p^{\beta-\alpha}(T_0)$ (J/mol·K)	$0.565+0.002(T - T_0)$		11

^a Superscript/subscripts w =water; 0 = reference state; β = empty hydrate lattice; α = ice phase; L = liquid phase.

2.3.4 Fugacity Based Models

The classical thermodynamics approach based on the concept of equality of fugacities between hydrate phase f_w^H and aqueous phase f_w^π has been developed recently by Chen and Guo²⁸⁻²⁹. Klauda and Sandler³⁰ also proposed a model based on equality of fugacity for a hydrate in equilibrium with aqueous or ice phase.

The number of empirically-fitted parameters is reduced due to the ability to predict one of its parameters by calculating the values of energy from computational quantum mechanics, as they correspond to the values at absolute zero temperature. The model uses Kihara potentials parameters calculated from viscosity and second virial coefficient data. The vapor pressure of empty hydrate is dependent on the guest molecule thereby increasing the ability to predict the phase equilibria more accurately. The method can be used for mixed hydrates and predict the phase equilibria and structure transitions without refitting the parameters. The shell radii are kept constant in calculating the cell potential to reduce the number of parameters and to reduce the computation time a single cavity is included in the calculations. The number of adjustable parameters is three per guest in a hydrate structure which are similar to that of the vdWP model.

2.3.5 The Cell Potential Method

Bazant and Trout³¹ proposed that the spherically-averaged intermolecular potential can be determined by the temperature-dependent Langmuir constant. Anderson et al.³² used Bazant's cell potential method where the guest-host interaction potentials are calculated analytically to determine the potential well depths and negative energy volumes for 16 guest components that form simple hydrates. They also extrapolated the cell potentials for a guest molecule in a known structure to estimate the cell potential in another hydrate structure. The parameters obtained are

verified by accurately predicting the phase equilibria of mixed hydrates without fitting to the experimental data.

In this work the cell potential code developed by Anderson et al.³² is modified for variable reference parameters. The Langmuir constants are determined using van't Hoff temperature dependence equation. The van der Waals equation⁶ is used to calculate the chemical potential difference of water in empty hydrate lattice and in hydrate phase. Then Holder et al.¹¹ equation with variable reference parameters is used to calculate the dissociation pressure. Therefore, the model used in this method is van der Waals model along with variable reference parameters to account for lattice distortion and cell potential code for calculating the Langmuir constants.

2.4 Methods Used in This Work for the Prediction of the Hydrate Phase Diagram

Gas gravity method and K_{vsi} value method are simple, but are developed before the knowledge of the hydrate structures, cannot be used for both structures. They could not predict the phase equilibria accurately. Klauda and Sandler³⁰ also have same no. of parameters as that of vdWP model. Therefore, in this work the van der Waal and Platteeuw⁶ model is used in calculating the chemical potential difference of water between the empty hydrate and the hydrate phase, $\Delta\mu_w^{\beta-H}(T, P)$. The cage occupancy and Langmuir constant are related by Langmuir adsorption isotherm, Langmuir constant is calculated using cell potential code as described in section 2.4.1. Holder et al.¹¹ simplified equation is used for calculating the chemical potential difference of water in empty hydrate and in aqueous phase, $\Delta\mu_w^{\beta-L,\alpha}(T, P)$.

Parrish and Prausnitz¹⁰ proposed an algorithm for the prediction of three-phase hydrate equilibrium curve that was further simplified by Holder et al.¹¹ in Equation 2.13 to eliminate the reference hydrate. This algorithm predicts the equilibrium pressure at a given temperature by an

iterative process until chemical potential difference calculated using Equations 2.6 and 2.13 are equal within the error tolerance.

The present model incorporates this algorithm for the prediction of three-phase equilibrium for both simple and mixed hydrates. An initial guess for the estimation of pressure is given by a simple experimental curve shown in Equation 2.19.

$$P_{eq} = \sum_{i=1}^n y_i \exp(A_i + \frac{B_i}{T}) \quad (2.19)$$

where y_i is the mole fraction of guest component in vapor phase, A_i and B_i are constants determined from the experimental data.

2.4.1 Determination of Langmuir Constants

To accurately predict the equilibrium pressure, the calculation of Langmuir constants is important. Bazant and Trout³¹ proposed that the spherically averaged intermolecular potential can be determined by the temperature-dependent Langmuir constant. The Langmuir constant values computed from experimental data (for hydrates that occupy only large cage) and *ab initio* data (for hydrates that occupy both cages) can be well fitted to van't Hoff temperature dependence given by:

$$C(\beta) = C_0 e^{m\beta} \quad (2.20)$$

where $\beta=1/KT$, C_0 and m are specific for each guest component J and cavity type i .

The two unknown parameters m and C_0 , known as cell potential parameters, are determined by regression of calculated Langmuir constants for a given guest over a wide range of temperatures. The cell potential parameters were determined from the simple hydrate experimental equilibrium data and are validated by predicting the phase equilibrium data of mixed hydrates without fitting

to the experimental data. Anderson et.al.³² accurately predicted the structure transition in methane-ethane mixture at $x_{CH_4}=0.74$. They also predicted a structure transition in methane-cyclopropane mixture at conditions outside the structure II region of cyclopropane.

In this work, the Langmuir constants are calculated using the cell potential parameters. Variable reference parameters based on the Holder¹¹ model are used for each guest component and reference parameters for mixed hydrates are calculated as mole fraction scaled reference parameters from the pure component reference parameters and is given as:

$$\text{Mixed hydrate reference parameter} = \sum_{i=1}^N \text{Reference parameter of } i \times y_i \quad (2.21)$$

The algorithm for the prediction of the equilibrium curves using cell potential method illustrated in Figure 2.1 and is as follows

1. Read the input parameters temperature and mole fraction of the guest components in vapor phase.
2. Read pure component properties and reference parameters which are used in the Equations 2.6 and 2.13.
3. Assume that the hydrate forms structure I.
4. The Langmuir constants are calculated.
5. The initial guess for pressure P_0 is estimated using Equation 2.18.
6. Fugacity of each component is calculated using the Peng-Robinson equation.
7. Activity coefficient of water is calculated from Henry's law.
8. Cage occupancies are calculated using Equation 2.11.
9. Configurational chemical potential is calculated using Equation 2.12.
10. Pressure, P_1 is calculated by Holder et.al. Equation 2.13.

11. If $P_1 = P_0$ then P_1 is the equilibrium pressure else the guess for P_0 is adjusted and process is repeated from step 6.
12. Assume structure II, and repeat the procedure for calculating the structure II equilibrium pressure, P_2 .
13. If $P_1 < P_2$ then the hydrate forms structure I at an equilibrium pressure of P_1 else it forms structure II at an equilibrium pressure of P_2 .

Figure 2.1 Schematic of Computer Program for Calculating Equilibrium Pressure.

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3 Estimation of Dissociation Pressure of CH₄-C₂H₆ Hydrates Using Empirical Correlations

3.1 Introduction

In the following sections two new empirical relationships for the calculation of gas hydrate phase equilibria are described. The predictions obtained using these empirical relationships are compared to any available experimental data. The correlations are validated by predicting the structural transitions that are known to occur.

For CH₄ hydrate in many reservoir simulators including HydrateResSim¹, TOUGH+Hydrate², MH-21³, and CMG STARS⁴ the relationship between the equilibrium pressure and the equilibrium temperature is given by a regression equation developed by Kamath⁵ and parameterized by Moridis⁶ while STOMP-HYD⁷ simulator incorporates the tabulated data of phase equilibrium. Instead of tabulated data it would be simple to develop an expression for binary hydrates to implement in the reservoir simulators, the dissociation pressure will be a function of both temperature and gas phase composition.

As discussed in chapter 2 there are three common techniques used to estimate the hydrate formation conditions

1. Gas gravity method
2. K_{vsi} -value Method
3. Statistical Thermodynamics approach.

The gas gravity method as discussed in chapter 2 is a simple method for estimating the hydrate formation conditions using the Katz gas gravity charts⁸. Though the method is simple it is not

accurate therefore it should be used only as a first estimate⁹. The Distribution Coefficient (K_{vsi} -value) Method developed by Wilcox et al.¹⁰ and confirmed by Carson and Katz¹¹ uses the K_{vsi} -value charts or equation are used to estimate the hydrate forming conditions. The technique used in the calculation of the equilibrium conditions involves the calculation of K_{vsi} value such that the sum of mole fraction of each component in the vapor phase divided by the K_{vsi} value equals unity, at the three- phase equilibrium conditions.

$$\sum_{i=1}^n \frac{y_i}{K_{vsi}} = 1.0 \quad (3.1)$$

The accuracy depends on the initial guess of the two pressures. If the pressures assumed are not within the range of the dissociation pressure then the predictions are not accurate. The method has many limitations hence a more accurate and simple method has to be developed for predicting the phase equilibria.

The statistical thermodynamics approach first developed by van der Waals and Platteeuw¹² is based on the criteria that at equilibrium the chemical potential of water in hydrate phase should be equal to the chemical potential of water in aqueous phase. This method involves a number of iterations in calculating the pressure such that the chemical potential of water in both phases is equal. This requires many of computational steps and can be time-consuming. In reservoir simulations, where there are large number of grid blocks, incorporation of statistical thermodynamics models takes a lot of time and steps for calculating the dissociation pressure of the gas hydrate in the reservoir. A method which is simple and fast as gas gravity and K_{vsi} methods and accurate as statistical thermodynamics approach has to be developed. Hence an empirical equation which can directly calculate the dissociation pressure at a particular temperature and gas phase composition is desired.

The dissociation pressure of hydrate can be correlated to the temperature and binary gas composition by an empirical correlation and the parameters in the correlation are obtained by linear regression analysis and non-linear regression analysis by fitting the data obtained from experimental data from Deaton and Frost¹³, McLeod and Campbell¹⁴ and Holder and Grigoriou¹⁵ and data obtained using cell potential code developed by Anderson et al¹⁶. The parameters obtained are validated by predicting the experimental data accurately.

3.2 Linear Regression Analysis:

In this work, the effect of gas composition and temperature on the dissociation pressure of the CH₄-C₂H₆ mixed hydrate is analyzed consecutively i.e.; effect of gas composition is studied first followed by the effect of temperature using linear regression analysis in Microsoft Excel.

The effect of the gas phase composition on the dissociation pressures is analyzed at different temperatures and a correlation is developed with respect to gas vapor composition and the dissociation pressure by fitting the predicted phase equilibrium data obtained from the cell potential code¹⁶.

$$\ln P = a + \frac{b}{(1+y)} + \frac{c}{(1+y)^2} + dy + ey^2 + fy^3 + gy^4 \quad (3.2)$$

where the coefficients a - g are calculated for both structure I and structure II.

The coefficients obtained in the above expression are function of temperature. A regression analysis is done for each parameter with respect to temperature and each coefficient is fit to a third degree polynomial in terms of temperature. For example, the parameter a is defined as

$$a = a_0 + a_1T + a_2 \times T^2 + a_3 \times T^3 \quad (3.3)$$

Similarly all other parameters are defined in terms of temperature and the dissociation pressure is defined as in Equation 3.4. The parameter values obtained by the analysis are listed in Table 3.1.

$$\ln P = \sum_{i=0}^3 a_i T^i + \frac{\sum_{i=0}^3 b_i T^i}{(1+y)} + \frac{\sum_{i=0}^3 c_i T^i}{(1+y)^2} + \sum_{i=0}^3 d_i T^i y + \sum_{i=0}^3 e_i T^i y^2 + \sum_{i=0}^3 f_i T^i y^3 + \sum_{i=0}^3 g_i T^i y^4 \quad (3.4)$$

Table 3.1 Coefficients of Empirical Equation by Microsoft Excel Analysis for Structure I and Structure II.

Coefficients	Structure I	Structure II
a_0	-2974804.965002	-270499654.173141
a_1	32132.921367	2924596.932978
a_2	-115.517876	-10537.502714
a_3	0.138237	12.653565
b_0	4006046.103327	0
b_1	-43277.358232	0
b_2	155.611589	0
b_3	-0.186262	0
c_0	-1032765.961111	287195690.822474
c_1	11160.846903	-3105100.722116
c_2	-40.152949	11187.828942
c_3	0.048097	-13.434434
d_0	1954799.754985	442911608.728495
d_1	-21110.944273	-4788727.188461
d_2	75.868424	17254.225412
d_3	-0.090748	-20.719269
e_0	-1018591.117651	-407251388.631463
e_1	10996.437916	4403236.955167
e_2	-39.493817	-15865.500506
e_3	0.047197	19.051941
f_0	341583.009439	208879257.437147
f_1	-3684.968990	-2258467.100300
f_2	13.216641	8137.748136
f_3	-0.015764	-9.772341
g_0	-48053.167468	-45841204.225972
g_1	517.526728	495662.228400
g_2	-1.850043	-1786.024048
g_3	0.002196	2.144830

Note: All the figures are significant.

At a specified temperature and vapor gas composition, dissociation pressure for both structures is calculated and the least of the two values is taken as the dissociation pressure and the structure as stable structure. The expression predicted the dissociation pressure with an average absolute deviation (AAD) of 5.91% from the experimental data from Deaton and Frost¹³, McLeod and Campbell¹⁴ and Holder and Grigoriou¹⁵. The experimental and predicted values of dissociation pressures at experimental data points are tabulated in Table 3.4.

The graph of the predicted pressure versus experimental pressure of the mixed hydrate of CH₄-C₂H₆ is shown in Figure 3.1. As evident from Figure 3.1 the predictions are not accurate at high pressures. The error from the experimental data is plotted against mole fraction of CH₄ in vapor phase in Figure 3.2, where it can be seen that the error percentage varies from +30% to -70%.

Figure 3.1 Predicted Pressure vs Experimental Pressure of CH₄-C₂H₆ Hydrate

Figure 3.2 Dissociation Pressure Error Percentage vs. Mole fraction of CH₄ in Vapor Phase for CH₄-C₂H₆ Hydrate.

The parameters of structure II expression do not predict the pressure well at mole fractions less than $y_{CH_4} = 0.58$, the predictions of structure I and structure II at 274.2 K are shown in Figure 3.3. Hence there is a need to develop a correlation with more accurate parameters that can predict the pressures in the entire range of gas mixture composition.

Figure 3.3 Pressure Predictions of CH₄-C₂H₆ Mixed Hydrate for Structure I and Structure II Using Empirical Equation Obtained by Regression Analysis Using Microsoft Excel at 274.2 K. The Structure with Low Dissociation Pressure is considered as Stable Structure.

3.3 Non- Linear Regression Analysis:

The non-linear regression analysis is done to study the effect of temperature and gas composition on the dissociation pressure of CH₄-C₂H₆ mixed hydrate simultaneously using SPSS package. The effects of gas composition and temperature are evaluated together where as in previous section the effects are evaluated successively. Non-linear regression analysis for multiple variables is performed on the data obtained from the experimental data weighted four times and the dissociation pressure data calculated using the cell potential code¹⁶ where the dissociation pressure is correlated to the temperature and the gas composition. The correlation obtained in the linear regression analysis using Microsoft Excel is used, and the results of the non-linear regression analysis for structure I and structure II are listed in Table 3.2 and Table 3.3 where the values of the coefficients are tabulated along with standard error within 95% confidence interval.

$$\ln P = \sum_{i=0}^3 a_i T^i + \frac{\sum_{i=0}^3 b_i T^i}{(1+y)} + \frac{\sum_{i=0}^3 c_i T^i}{(1+y)^2} + \sum_{i=0}^3 d_i T^i y + \sum_{i=0}^3 e_i T^i y^2 + \sum_{i=0}^3 f_i T^i y^3 + \sum_{i=0}^3 g_i T^i y^4 \quad (3.5)$$

Table 3.2 Coefficients of Empirical Expression by SPSS analysis for Structure I

Parameter Estimates				
Parameter	Estimate	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
a_0	17881.790	60971.551	-102126.325	137889.905
a_1	347.471	544.293	-723.843	1418.784
a_2	.114	1.956	-3.736	3.964
a_3	-.005	.003	-.012	.001
b_0	-1209.148	6097.588	-13210.811	10792.515
b_1	-67.885	400.548	-856.270	720.501
b_2	-3.803	2.781	-9.277	1.671
b_3	.014	.006	.003	.025
c_0	-8347.489	62558.026	-131478.206	114783.229
c_1	-374.736	710.306	-1772.806	1023.333
c_2	4.050	2.827	-1.514	9.614
c_3	-.009	.004	-.017	-.002
d_0	-6644.378	118037.836	-238974.016	225685.259
d_1	-850.776	1143.231	-3100.956	1399.403
d_2	4.096	3.790	-3.364	11.556
d_3	-.004	.005	-.013	.005
e_0	12360.186	201058.493	-383376.029	408096.402
e_1	861.480	2094.779	-3261.599	4984.560
e_2	-5.371	7.396	-19.928	9.186
e_3	.008	.009	-.010	.025
f_0	-47184.571	264944.675	-568665.666	474296.524
f_1	-112.566	2833.409	-5689.463	5464.331
f_2	2.116	10.157	-17.876	22.109
f_3	-.004	.012	-.028	.020
g_0	31495.977	139246.281	-242577.482	305569.435
g_1	-173.921	1497.968	-3122.318	2774.476
g_2	.133	5.383	-10.461	10.728
g_3	.000	.006	-.012	.013

Table 3.3 Coefficients of Empirical Expression by SPSS analysis for Structure II

Parameter Estimates				
Parameter	Estimate	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
a_0	7079.661	307346.229	-597858.892	612018.214
a_1	785.101	961.507	-1107.400	2677.601
a_2	-2.477	7.687	-17.608	12.654
a_3	-.001	.020	-.041	.039
b_0	12181.914	314809.415	-607446.161	631809.989
b_1	-124.077	704.182	-1510.094	1261.941
b_2	-4.099	12.759	-29.212	21.015
b_3	.015	.030	-.043	.074
c_0	-9237.976	63717.811	-134651.457	116175.506
c_1	-774.979	1007.537	-2758.079	1208.120
c_2	7.006	6.039	-4.881	18.893
c_3	-.015	.010	-.035	.006
d_0	-2453.910	300470.862	-593859.924	588952.104
d_1	-1602.056	1714.144	-4975.945	1771.833
d_2	9.242	5.328	-1.245	19.729
d_3	-.013	.012	-.037	.012
e_0	4000.624	280661.624	-548415.578	556416.826
e_1	1858.739	2406.869	-2878.615	6596.094
e_2	-12.164	7.959	-27.829	3.500
e_3	.020	.011	-.002	.041
f_0	-28166.965	266746.364	-553194.261	496860.331
f_1	-997.563	2782.675	-6474.602	4479.475
f_2	7.722	9.976	-11.913	27.356
f_3	-.014	.012	-.038	.011
g_0	21519.789	131887.037	-238068.732	281108.311
g_1	150.124	1419.134	-2643.107	2943.354
g_2	-1.806	5.123	-11.889	8.278
g_3	.004	.006	-.009	.016

The parameters values have to be used along with all significant numbers to predict the values accurately. The predictions along with experimental data are listed in Table 3.4.

Table 3.4 Experimental and Predicted Dissociation Pressures at Various Temperatures and Gas Phase Composition of CH₄-C₂H₆ Hydrate.

%CH ₄	Temperature (K)	Experimental P(Bar)	Predicted P(Bar) Linear Regression Analysis(LRA)	Predicted P(Bar) Non-Linear Regression Analysis(NLRA)	Absolute Error (%) (LRA)	Absolute Error (%) (NLRA)
1.6	283.9	18.1	19.02	19.12	5.08287	5.63536
1.6	285.7	23.1	24.56	23.81	6.3203	3.07359
1.6	286.6	27.1	28.03	26.33	3.43473	2.84133
1.6	287.8	30.8	33.64	29.74	9.22077	3.44156
4.7	279.4	9.9	10.55	10.61	6.56565	7.17172
4.7	281.5	13.4	13.77	13.95	2.76119	4.10448
4.7	283.3	17.1	17.43	17.51	1.92982	2.39766
4.7	285.3	21.7	22.87	22.07	5.39170	1.70507
4.7	286.4	25.1	26.69	24.72	6.33466	1.51395
4.7	287.6	29.9	31.74	27.57	6.15384	7.79264
17.7	281.6	14.2	14.46	14.59	1.83098	2.74648
17.7	283.3	17.7	17.82	18.01	0.67796	1.75141
17.7	284.8	21.4	21.5	21.46	0.46729	0.28037
17.7	286.2	26.6	25.73	24.92	3.27067	6.31579
17.7	287	30	28.56	26.93	4.80	10.23333
56.4	274.8	9.45	8.12	9.26	14.07407	2.01058
56.4	277.6	12.89	11.49	12.48	10.86113	3.18076
56.4	280.4	17.58	16.25	17.32	7.54542	1.47895
56.4	283.2	24.34	22.52	23.91	7.47740	1.76664
90.4	274.8	15.24	15.98	16.59	4.85564	8.85827
90.4	277.6	20.96	21.64	22.58	3.24428	7.72901
90.4	280.4	28.89	29.42	31.24	1.83455	8.13430
90.4	283.2	39.65	40.31	42.49	1.66457	7.16267
95	274.8	18.41	20.11	22.89	9.23411	24.33460
95	277.6	25.3	27.22	30.89	7.58893	22.09486
95	280.4	34.47	37.12	42.08	7.68785	22.07717
95	283.2	47.71	51.001	57.05	6.89793	19.57661
97.1	274.8	21.58	25.02	35.98	15.94069	66.72845
97.1	280.4	40.34	45.85	46.09	13.65890	14.25384
97.8	274.8	23.65	26.98	26.94	14.08034	13.91121
97.8	280.4	44.13	47.39	47.59	7.38727	7.84047
97.8	283.2	60.88	63.62	64.31	4.50066	5.63403
98.8	274.8	28.61	28.49	28.43	0.41943	0.62915
98.8	277.6	38.06	37.52	37.03	1.41881	2.70625
98.8	280.4	50.88	49.75	49.88	2.22091	1.96541
				AAD (%)	5.91007	8.659371

The non-linear regression expression predicted the pressures with an AAD of 8.98% from the experimental data from Deaton and Frost¹³, McLeod and Campbell¹⁴ and Holder and Grigoriou¹, where as the cell potential code developed by Anderson et al.¹⁶ predicted with an AAD% of 5.96% and the CSMGEM developed by Sloan et al.⁹ with an AAD% of 6.58%. The predicted pressure by the correlation and the cell potential code is plotted against experimental pressure of the mixed hydrate of CH₄-C₂H₆ as shown in Figure 3.4 the predictions are close to the predictions of cell potential code. Figure 3.5 is the deviation from the experimental data with respect to the mole fraction of CH₄ in vapor phase.

Figure 3.4 Predicted Pressure vs. Experimental Pressure for CH₄-C₂H₆ Hydrate.

Figure 3.5 Dissociation Pressure Error Percentage vs Mole fraction of CH₄ in Vapor Phase for CH₄-C₂H₆ Hydrate .

It has been found experimentally that the CH₄-C₂H₆ mixed hydrate undergoes a structural transition from structure I to structure II at a methane mole fraction between 0.72- 0.75 in vapor phase at 274.2 K and the structure reverts from structure II to structure I at 0.992-0.994 mole fraction of methane¹⁷⁻¹⁸, the expression predicts the structural transition from structure I to structure II at 0.72-0.73 mole fraction of CH₄ in vapor phase at 274.2 K, while that from structure II to structure I at 0.95-0.96 mole fraction of methane as given in Figure 3.6.

Figure 3.6 Pressure Predictions of CH₄-C₂H₆ Mixed Hydrate for Structure I and Structure II Using Expression Obtained by Non-linear Regression Analysis Using SPSS at 274.2 K. The Structure with Low Dissociation Pressure is Considered as Stable Structure.

3.4 Conclusions

The empirical expressions derived in this work and described in this chapter can be used in reservoir simulations for estimating the dissociation pressures of the gas hydrates. The parameters for the empirical expression were determined for CH₄-C₂H₆ hydrate by linear regression analysis using Microsoft Excel and by a non-linear regression analysis using SPSS. Dissociation pressures are calculated and compared with any available experimental data. The expression obtained by linear regression analysis though predicted the experimental data well, it could not predict the pressures for structure II for CH₄ vapor phase composition less than $x_{CH_4} = 0.58$. The expression obtained by the non-linear regression analysis predicted the pressure with an AAD of 8.98% and structural transitions are predicted to occur at 0.72-0.73 mole fraction of

methane in vapor phase at 274.2 K. This is in agreement with the experimental data and the upper transition at 0.95-0.96 mole fraction of methane which implies a trace amount of ethane is sufficient for transition of structure from structure II to structure I. The equations could be implemented into the reservoir simulators allowing for the calculation of dissociation pressures at various reservoir temperatures and gas phase compositions for both the structures. The stable structure is determined as the structure with lowest dissociation pressure. The estimation of pressures is quite simple and fast, though the predictions are not accurate they can be used as a first estimate. The correlations could not predict the cage occupancies and hydrate phase compositions, which is important to estimate the amount of gas is stored in the hydrate. In statistical thermodynamics approach pressure is calculated by an iterative process, which requires lot of computational steps and time but the algorithm can predict the cage occupancies and hydrate phase composition along with the dissociation pressure. Hence for an easy and fast estimation of the dissociation pressure in the reservoir simulations the empirical equation can be used but for an accurate prediction and for hydrate phase composition the empirical correlation is not a solution. Therefore, there is a need to develop a method which is more accurate and can be implemented in to the reservoir simulators. van der Waals model with Langmuir constants being calculated from the van't Hoff temperature and with variable reference parameters can be a solution.

3.5 References

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4 Phase Equilibrium Predictions of Gas Hydrates Using Cell Potential Code

4.1 Introduction

In spite of the large experimental data¹ base of clathrate phase behavior, the theory of clathrate phase behavior is not well developed and still depends on ad hoc fitting of the experimental data. However the fitting procedures cannot produce accurate results outside the range of fitting. The reference parameters used in these methods while fitting the intermolecular potential parameters to the experimental data^{1, 2} obtained by numerically fitting procedures differs from the values determined experimentally³ or computationally⁴ and they are also needed to be adjusted² to predict the phase equilibrium and structural transitions.

Recently, Bazant and Trout⁵ proposed that the spherically averaged intermolecular potential can be determined by the temperature dependent Langmuir constant. The cell potential parameters are determined directly from the experimental equilibrium data by analytically solving the integral equation based on van der Waals and Platteeuw⁶ statistical thermodynamics model.

$$C(\beta) = 4\pi\beta \int_0^\infty e^{-\beta w(r)} r^2 dr \quad (4.1)$$

where $\beta = 1/kT$, k = Boltzmann constant and T = Temperature (K).

The Langmuir constant values computed from experimental data (for hydrates that occupy only large cage) and *ab initio* data (for hydrates that occupy both cages) can be well fitted to van't Hoff temperature dependence given by:

$$C(\beta) = C_0 e^{m\beta} \quad (4.2)$$

where C_0 and m are specific for each guest component J and cavity type i

Combining Equations 4.1 and 4.2 yields an integral equation of the form

$$C_0 e^{m\beta} = 4\pi\beta \int_0^\infty e^{-\beta w(r)} r^2 dr \quad (4.3)$$

There are infinite numbers of solutions to the above integral equation, all but one central-well solution are aphysical with discontinuities and cusps in the potentials. Hence the central-well solution to Equation 4.3 is selected to represent van't Hoff temperature dependence given in Equation 4.2.

$$C_{ji}(\beta) = \beta F(\beta) e^{-w(r_0)\beta} \quad (4.4)$$

where

$$F(\beta) = \beta \int_0^\infty e^{-\beta y} g(y) dy \quad (4.5)$$

and $g(y)$ is the inverse Laplace transform of the function given by

$$G(\beta) = \frac{F(\beta)}{\beta} = \frac{C(\beta) e^{\beta w_0}}{\beta^2} \quad (4.6)$$

which leads to the general expression for the central-well potential $w(r)$ as:

$$w(r) = w_0 + g^{-1}\left(\frac{4}{3}\pi r^3\right) \quad (4.7)$$

For the perfect van't Hoff behavior, $F(\beta)$ and $G(\beta)$ are given as:

$$\left. \begin{aligned} F(\beta) &= C_0/\beta \\ G(\beta) &= C_0/\beta^2 \end{aligned} \right\} \quad (4.8)$$

The inverse Laplace transforms for these functions are given as

$$\left. \begin{aligned} f(y) &= C_0 H(y) \\ g(y) &= C_0 y H(y) \end{aligned} \right\} \quad (4.9)$$

where $H(y)$ is the Heaviside step function. Thus, the unique central-well solution for Equation 4.3 is:

$$w(r) = \frac{4\pi r^3}{3C_0} - m \quad \text{for } r \geq 0 \quad (4.10)$$

The Langmuir constant values are well fitted to van't Hoff temperature dependence linear plot defined as:

$$\log C = m\beta + \log C_0 \quad (4.11)$$

where the slope of van't Hoff plot, m equals the well depth, $-w(0)$, and the y-intercept, $\log C_0$ is related to the well size measured as volume of negative energy, mC_0 with corresponding spherical radius given as:

$$r_s = \left(\frac{3mC_0}{4\pi} \right)^{1/3} \quad (4.12)$$

Finally, the cell potential is simplified as:

$$w(r) = m \left[\left(\frac{r}{r_s} \right)^3 - 1 \right] \quad \text{for } r \geq 0 \quad (4.13)$$

The two unknown parameters m and C_0 known as cell potential parameters are determined by regression of calculated Langmuir constants for a given guest over a wide range of temperatures.

4.1.1 Langmuir Constants

Langmuir constants can be calculated from the experimental phase equilibrium data for the simple gas hydrates that occupy only one type of cages, like ethane, cyclopropane, propane and isobutane which occupies only the large cage of the hydrate structure. For the hydrates which occupy both the cages, Langmuir constants can be calculated using *ab initio* potentials such as those developed by Cao et al.⁷ and Anderson et al.⁸

For Single Occupancy Hydrates:

The van der Waals and Platteeuw⁶ equation for the chemical potential difference between water in empty hydrate lattice and the hydrate phase is given by

$$\Delta\mu_w^{\beta-H}(T, P) = kT \sum_i v_i \ln (1 + C_{ji}f_j) \quad (4.14)$$

For single occupancy in large cage the above equation reduces to

$$\text{for structure I : } \frac{\Delta\mu_w^{\beta-H}(T, P)}{kT} = \frac{3}{23} \ln(1 + C_{J2}f_J) \quad (4.15)$$

$$\text{for structure II: } \frac{\Delta\mu_w^{\beta-H}(T, P)}{kT} = \frac{1}{17} \ln(1 + C_{J2}f_J) \quad (4.16)$$

The Langmuir constants are obtained by solving for the C_{J2} values in Equations 4.15 and 4.16, and using the fact that at equilibrium $\Delta\mu_w^{\beta-H}(T, P) = \Delta\mu_w^{\beta-L, \alpha}(T, P)$

Therefore,

$$\text{for structure I : } C_{J2} = \frac{\exp\left(\frac{23}{3}\Delta\mu_w^{\beta-L, \alpha}/kT\right)-1}{\hat{f}_J} \quad (4.17)$$

$$\text{for structure II: } C_{J2} = \frac{\exp\left(\frac{17}{1}\Delta\mu_w^{\beta-L, \alpha}/kT\right)-1}{\hat{f}_J} \quad (4.18)$$

where $\hat{f}_j$ is calculated using Peng-Robinson⁹ equation of state and $\Delta\mu_w^{\beta-L,\alpha}$ using equation proposed by Holder et al.¹⁰

$$\frac{\Delta\mu_w^{\beta-L,\alpha}(T,P)}{KT} = \frac{\Delta\mu_w^{\beta-L,\alpha}(T_0,0)}{KT} - \int_{T_0}^T \left[\frac{\Delta h_w^{\beta-L,\alpha}(T)}{KT^2} \right] dT + \int_0^P \left[\frac{\Delta V_w^{\beta-L,\alpha}}{KT} \right] dP - \ln a_w^L \quad (4.19)$$

For Hydrates Occupying Both Cages:

The *ab initio* potential method is used to calculate the Langmuir constants for hydrates that occupy both large and small cages at various temperatures by integrating the full 6-dimensional configurational integral over 5 hydrate shells. This method not only allows calculating the Langmuir constants of the stable structure but also for the unstable structure. Using this method Langmuir constants are calculated for methane and argon by Anderson et al.⁸ and for carbon dioxide by Velaga and Anderson¹¹ for both structures.

4.2 Reference Parameters

The reference chemical potential difference $\Delta\mu_w^0$ and reference enthalpy difference Δh_w^0 are essential input parameters for calculating phase equilibrium data using statistical thermodynamics model. Several methods, both experimental and empirical are adopted in past to determine the reference parameters. Holder et al.¹⁰ developed an empirical correlation method to calculate the reference chemical potential difference, $\Delta\mu_w^0$ and reference enthalpy difference, Δh_w^0 and they calculated the reference parameters for structure I hydrate using the cyclopropane data of Dharmawardhana et al.¹² The values given by earlier researchers for structure I and structure II are tabulated in Table 2.1. Later Hwang et al.¹³ by molecular dynamic simulations on unit cell of gas hydrates with different guest molecules proposed that the guest molecules have impact on host-host interactions in the lattice hence the reference parameters

should vary with the guest molecule. Reference parameters for methane for structure I and for argon for structure II were developed by Anderson et al.⁴ and for carbon dioxide for structure I are determined by Velaga and Anderson.¹¹ The values are tabulated in Table 4.1.

Table 4.1 Reference Parameter Values Determined by *Ab Initio* Intermolecular Potentials

Component	Structure	$\Delta\mu_w^0$ J/mol	Δh_w^0 J/mol
Methane	Structure I	1203 $\pm$ 3	1179 $\pm$ 19
Argon	Structure II	1077 $\pm$ 5	1294 $\pm$ 11
Carbon dioxide	Structure I	1204 $\pm$ 3	1190 $\pm$ 12

Zele et al.¹⁴ developed an empirical correlation between reference chemical potential and the cavity radius given by

$$R = A + B \times \Delta\mu_w^0 \quad (4.20)$$

where R is the radius in Å and $\Delta\mu_w^0$ is in cal/mol. A and B are constants for three water shells for each type of cavity. Lee and Holder¹⁵ developed correlation equations for $\Delta\mu_w^0$ (cal/mol) and the Kihara hard-core parameter, a (pm), for structure I and structure II:

$$\left. \begin{array}{l} \text{for Structure I } \Delta\mu_w^0 = 133.39 \exp(0.0213 \times a), \quad R^2 = 0.9058 \\ \text{for Structure II } \Delta\mu_w^0 = 171.91 \exp(0.0101 \times a), \quad R^2 = 0.8810 \end{array} \right\} \quad (4.21)$$

The Kihara parameters are obtained by fitting to the viscosity or second virial coefficient data. The values obtained by Holder¹⁵ using these correlations for CH₄, CO₂ in structure I hydrate are 1083 J/mol and 2265 J/mol respectively and for Ar in structure II hydrate is 1037 J/mol which are not in agreement with the experimentally determined values of CH₄ hydrate 1203 J/mol by Anderson et al.⁸, CO₂ hydrate by Velaga and Anderson¹¹ 1204 J/mol and Ar hydrate 1077 J/mol

by Anderson et al.⁸ Therefore, a new correlation has to be determined in order to calculate the reference parameters more accurately.

In this work an empirical correlation is developed directly between the reference parameters and the molecular diameter of the guest molecules using linear regression analysis and the values are validated by predicting the phase equilibrium data of simple hydrates.

$$\left. \begin{array}{l} \text{for Structure I} \quad \Delta\mu_w^0 = 1197.279187 \exp(0.0010933 * d_g) \\ \quad \quad \quad \Delta h_w^0 = 1061.588965 \exp(0.022302 * d_g) \end{array} \right\} \quad (4.22)$$

$$\left. \begin{array}{l} \text{for Structure II} \quad \Delta\mu_w^0 = 1007.394579 \exp(0.0175821 * d_g) \\ \quad \quad \quad \Delta h_w^0 = 1179.046815 \exp(0.0244821 * d_g) \end{array} \right\} \quad (4.23)$$

where d_g is the molecular diameter of the guest molecule (Å), $\Delta\mu_w^0$ and Δh_w^0 are reference chemical potential and enthalpy difference respectively (J/mol).

The reference parameters are calculated for different guest molecules using the above empirical equations and the parameters are validated by reproducing the phase equilibrium data of simple gas hydrates using the cell potential method. The phase equilibrium conditions for mixed hydrates are calculated without adjusting any parameters. The reference parameters for mixed hydrates are calculated from the pure component parameters by using mixing rules

$$\left. \begin{array}{l} \Delta\mu_{w,mix}^0 = \sum_{i=1}^N \Delta\mu_{w,i}^0 \times y_i \\ \Delta h_{w,mix}^0 = \sum_{i=1}^N \Delta h_{w,i}^0 \times y_i \end{array} \right\} \quad (4.24)$$

where y_i gas phase composition of i component and N is the no. of guest components.

An entropy correction term is added to the mixture reference chemical potential difference is given by

$$\Delta\mu_{w,correction}^0 = \sum_{i=1}^N \sum_{j=1}^N |\Delta\mu_{w,i}^0 - \Delta\mu_{w,j}^0| \times z_i \times z_j \times ent_{correction} \quad (4.25)$$

where z_i is the hydrate phase composition of i component and $ent_{correction}$ is the entropy correction factor which accounts for the difference in the reference chemical potential values of the guest components and is taken as 86 for structure I hydrate and 4 for structure II hydrate.

4.3 Prediction of Phase Equilibrium Data of Gas Hydrates

In order to predict the phase equilibrium conditions for simple and mixed hydrates at any given temperature and gas composition, the algorithm discussed in Section 2.2 is used in an iterative manner to obtain the converged pressures that satisfies the van der Waals and Platteeuw⁶ model. The reference parameters are assumed to vary with the guest molecule, the Langmuir constants are calculated using cell potential parameters and the fugacity is determined by Peng-Robinson⁹ equation of state. The values of thermodynamic reference properties used in the algorithm are listed in Table 2.2. The schematic flow sheet for the predicting the equilibrium pressure at a particular temperature and gas composition is given in Figure 2.1.

4.3.1 Phase Equilibrium Predictions of Simple Gas Hydrates

The phase equilibrium data is predicted using cell potential code and the average absolute deviation (AAD) is calculated using the formula given by

$$\text{AAD \%} = 100 \times \frac{1}{N} \sum_{i=1}^N \frac{|P_{\text{exp}} - P_{\text{pred}}|}{P_{\text{exp}}} \quad (4.26)$$

where N= no. of data points.

The predictive ability of the cell potential method can be verified against experimental structural transitions that are known to occur. For example, cyclopropane undergoes a structure transition as a function of temperature, it forms structure II hydrate at temperatures between 257.1 and 274.6 K¹⁶ and structure I otherwise. Using this method, the transitions are predicted to occur at 256.4 and 274.6 K respectively as shown in Figure 4.1.

Figure 4.1 Cyclopropane (C-C₃H₆) Structural Transitions. Vertical Lines Indicate the Structural Transition Boundaries.

Average absolute deviations are calculated for various simple hydrates and are compared with those calculations of CSMGEM¹ a widely used code available from the Text “Clathrate Hydrates of natural Gases.” These are given in Figure 4.2. Phase equilibrium calculations of cyclopropane cannot be calculated using the CSMGEM¹ software.

Figure 4.2 Comparison of Average Absolute Deviations from Experimental Data for Simple Hydrates Predicted by This Model and CSMGEM Software.

The average absolute difference is more for this model when compared to that of CSMGEM, mainly because of the equation of state used to calculate the fugacity, Peng-Robinson⁹ equation could not calculate the fugacities accurately for high pressures, but the occupancies predicted by this model are more realistic when compared to that of CSMGEM¹. For example, CSMGEM¹ predicted the phase equilibrium of carbon dioxide hydrate accurately but it over estimates the small cage occupancies. The cage occupancy for carbon dioxide hydrate using the experimental

techniques reported that the large cage is almost fully occupied, but there is a large inconsistency about the small cage occupancy¹⁷⁻¹⁹. Because of the relative sizes of the carbon dioxide and small cage, it was assumed that the small cage is unoccupied. Ripmeester and Ratcliffe¹⁹ used solid state NMR and found that the carbon dioxide indeed occupies the small cage and they measure the occupancy ratio from the spectra θ_s/θ_L as 0.32, giving a lower limit to the hydration number (no. of water molecules per guest molecule) for CO₂ hydrate of 7.0. CSMGEM predicts occupancy between 45 to 70% in small cages and 96 to 98% in large cages while this work predicts around 20 to 35% in small cages and 98 to 99% in large cages for temperatures ranging 151.5 to 283.3 K which are in agreement with the experimental data point given by Ripmeester and Ratcliffe. The hydration numbers predicted by this method and CSMGEM at various temperatures are plotted in Figure 4.3, the values predicted by this method are above the lower limit given by Ripmeester and Ratcliffe¹⁹ while the values obtained from CSMGEM are below the reference point.

Figure 4.3 Hydration Number for CO₂ Hydrate Obtained by This Method and CSMGEM.

4.3.2 Phase Equilibrium Predictions of Binary Gas Hydrates

Natural gas hydrates can be formed either from the methane produced by bacterial activity at shallow depths^{1, 20-21} or by the thermal pyrolysis of fossil organic matter which contains methane as well as significant amounts of other higher hydrocarbons (C2-C5) and other non-hydrocarbon gases²². To understand the production of CH₄ from the hydrate it is important to accurately predict the phase equilibrium of the mixed hydrates. In this work, the phase equilibria of many different binary mixed hydrates such as CH₄-C₂H₆, CH₄-CO₂, CH₄-N₂ and N₂-CO₂ have been predicted so as to assess the production of the CH₄ from natural gas hydrate reservoirs formed by thermogenic gases for example the hydrates found in Gulf of Mexico consists of large crystal forms of hydrate which can contain methane and other hydrocarbons²³ and to understand the swapping of CH₄ in hydrate reservoirs by CO₂ and CO₂-N₂ gases.

4.3.2.1 CH₄-C₂H₆ Mixed Hydrate

The phase equilibria of the binary hydrate CH₄-C₂H₆ are predicted using this method, the three-dimensional phase diagram is shown in Figure 4.4 and the predictions are tabulated and compared with CSMGEM predictions in Table 4.2.

Figure 4.4 The Three-dimensional P - T - y Phase Diagram of Methane-Ethane (CH_4 - C_2H_6) Hydrate System.

Table 4.2 Phase Equilibrium Predictions of CH_4 - C_2H_6 Hydrate System by This Model and CSMGEM.

% CH_4	Temperature (K)	Experimental P(Bar)	This Model P(Bar)	CSMGEM P(Bar)	Absolute Error % (This Model)	Absolute Error% (CSMGEM)
1.6	283.9	18.1	19.0309	18.371	5.14309	1.49724
1.6	285.7	23.1	24.7395	23.689	7.0974	2.54978
1.6	286.6	27.1	28.5162	27.131	5.22583	0.11439
4.7	279.4	9.9	10.8649	10.219	9.74646	3.22222
4.7	281.5	13.4	14.1869	13.294	5.87239	0.79104
4.7	283.3	17.1	17.9784	16.756	5.13684	2.0117
4.7	285.3	21.7	23.7368	21.905	9.38618	0.9447
4.7	286.4	25.1	27.9624	25.583	11.404	1.9243
17.7	281.6	14.2	16.3292	13.864	14.9944	2.3662
17.7	283.3	17.7	20.2096	17.058	14.1785	3.62712
17.7	284.8	21.4	24.5671	20.572	14.7995	3.86916

17.7	286.2	26.6	29.7518	24.64	11.8489	7.36842
17.7	287	30	33.4004	27.41	11.3347	8.63333
56.4	274.8	9.45	11.1412	8.9867	17.8963	4.90265
56.4	277.6	12.89	15.2311	12.299	18.1621	4.58495
56.4	280.4	17.58	20.9696	16.889	19.281	3.9306
56.4	283.2	24.34	29.2768	23.375	20.2827	3.96467
80.9	288.8	70	69.9329	66.802	0.09586	4.56857
80.9	296.4	234.8	245.653	216.19	4.62232	7.92589
80.9	299	356.1	377.598	325.35	6.03701	8.63521
80.9	301.3	486.4	528.197	449.67	8.59311	7.5514
80.9	303.1	619.5	651.669	565.06	5.19275	8.78773
80.9	304.1	685.7	735.885	635.99	7.31881	7.24953
90.4	274.8	15.24	17.1432	15.807	12.4882	3.72047
90.4	277.6	20.96	23.1972	21.568	10.6737	2.90076
90.4	280.4	28.89	31.4999	29.481	9.03392	2.04569
90.4	283.2	39.65	43.2968	40.56	9.19748	2.29508
94.6	289.7	138.9	127.371	110.2	8.3	20.6623
94.6	293.6	242.4	228.423	203.23	5.76601	16.1592
94.6	296.6	344.4	349.807	331.81	1.56989	3.65563
94.6	299.1	482.3	479.212	480.24	0.64037	0.42712
94.6	301.2	622.3	618.189	616.71	0.66069	0.89828
94.6	302	684.3	678.613	741.7	0.83104	8.38813
95	274.8	18.41	21.3558	19.144	16.0011	3.98696
95	274.8	18.41	21.3558	19.144	16.0011	3.98696
95	277.6	25.3	28.8575	26.025	14.0613	2.86561
95	280.4	34.47	39.2955	35.525	13.9991	3.06063
95	283.2	47.71	54.306	48.949	13.8252	2.59694
97.1	274.8	21.58	25.5049	22.147	18.1877	2.62743
97.1	277.6	29.58	34.4621	30.043	16.5047	1.56525
97.1	280.4	40.34	46.8136	40.994	16.0476	1.62122
97.8	274.8	23.65	27.3073	23.657	15.4643	0.0296
97.8	277.6	32.27	36.1044	32.059	11.8822	0.65386
97.8	280.4	44.13	48.1477	43.732	9.10424	0.90188
97.8	282.6	56.68	60.7398	56.291	7.16267	0.68631
97.8	283.2	60.88	64.8087	60.417	6.45319	0.76051
98.8	274.8	28.61	28.7026	26.72	0.32366	6.60608
98.8	277.6	38.06	37.8127	36.122	0.64976	5.09196
98.8	280.4	50.88	50.214	49.22	1.30896	3.26258
80.9	291.7	104.5	107.29	100.32	2.66938	4
80.9	293.3	138.9	140.867	128.98	1.41605	7.14183
				AAD(%)	9.29164	4.18861

Interestingly, both CH_4 , and C_2H_6 form a structure I hydrate when the gas phase contains only one component but the $\text{CH}_4\text{-C}_2\text{H}_6$ mixed hydrate forms structure II at various gas mixture compositions. The mixed gas hydrate undergoes a transition from structure I to structure II at a methane gas phase mole fraction between 0.72 and 0.75 and the upper transition from structure II to structure I occurs at methane gas phase mole fraction between $0.992(\pm 0.005)$ - $0.994(\pm 0.007)$ at 274.2 K²⁷⁻²⁸. In this work the structural transitions from structure I to structure II at 0.72 and from structure II to structure I at 0.98 at 274.2 K. The structural transitions are shown in Figure 4.5. The predicted values are not so accurate, this may be due to the values of reference parameters of both components in structure II.

Figure 4.5 Methane-Ethane ($\text{CH}_4\text{-C}_2\text{H}_6$) Structural Transition Predictions at 274.2 K. Vertical Lines Indicate the Structural Transition Boundaries.

4.3.2.2 CH₄-CO₂ Mixed Hydrate

A new proposed method of production of CH₄ from the natural gas hydrate is by injection of CO₂ into reservoir. CO₂ sequestration in natural-gas-hydrate reservoirs by replacing the CH₄ is potentially attractive as it serves the dual purpose of long-term storage of a greenhouse gas (CO₂) and the production of natural gas (CH₄). Lee et al.²⁹ verified that the amount of CH₄ that could be recovered from the structure I CH₄ hydrate using CO₂ could reach 64% of the hydrate composition. In order to understand the replacement process it is essential to know the phase equilibrium conditions of the CH₄-CO₂ binary hydrate. Both CH₄ and CO₂ form structure I hydrate and the mixture of CH₄-CO₂ hydrate also forms structure I hydrate. CO₂ prefers to occupy large cages over small cages of structure I because of its molecular diameter being almost equal to the diameter of the small cage. The phase equilibria of CH₄-CO₂ hydrate are predicted and verified using the already existing experimental data³⁰⁻³¹. Figure 4.6 represents the three-dimensional phase equilibrium diagram. The occupancies obtained are more realistic, and the occupancy data have been sent to PNNL and are currently incorporated into STOMP-HYD³² simulator. The predictions are compared to CSMGEM¹ data along with experimental data³⁰⁻³¹ in Table 4.3. The dissociation pressure error is calculated and is plotted against the mole fraction of CH₄ in gas phase in Figure 4.7. The AAD for the cell potential method is 2.04% compared to 1.977% for CSMGEM.

Figure 4.6 The Three-dimensional P - T - y Phase Diagram of Methane-Carbon dioxide (CH_4 - CO_2) Hydrate System.

Table 4.3 Phase Equilibrium Predictions of CH_4 - CO_2 Hydrate System by This Model and CSMGEM.

% CH_4	Temperature (K)	Experimental P(Bar)	This Model P(Bar)	CSMGEM P(Bar)	Absolute Error % (This Model)	Absolute Error% (CSMGEM)
66	277	28.4	28.1496	28.046	0.88169	1.24648
70	278.9	34.6	35.7427	35.764	3.3026	3.36416
64	278.9	34.3	34.0184	34.208	0.82099	0.26822
68	280.9	42.4	43.8651	44.284	3.45542	4.4434
72	282.9	51.7	57.1329	57.543	10.5085	11.3017
40	275.5	19.9	19.8873	19.726	0.06382	0.87437
56	279.2	30.8	33.1108	33.501	7.5026	8.76948
87.5	276.4	32	32.3542	31.668	1.10688	1.0375
91.5	278.4	39.5	41.0616	40.58	3.95342	2.73418
93	281	51	54.2609	54.217	6.39392	6.30784

29	279.6	30	29.9539	30.091	0.15367	0.30333
39	282.2	42.7	42.7545	43.791	0.12763	2.55504
90	273.7	25.2	25.3504	24.529	0.59683	2.6627
91	275.8	31	31.4768	30.788	1.53806	0.68387
92	277.8	38.3	38.7875	38.283	1.27285	0.04439
92	280.2	49.1	49.6034	49.336	1.02525	0.48065
86	274.6	25.9	26.6038	25.841	2.71737	0.2278
87	276.9	32.4	33.8675	33.222	4.52932	2.53704
87	279.1	41.8	42.4766	41.989	1.61866	0.45215
87	281.6	53.8	55.3513	55.148	2.88346	2.50558
75	273.8	21.2	21.9158	21.36	3.37642	0.75472
78	279.4	39.6	40.427	40.251	2.08838	1.64394
78	283.4	62.3	63.4857	63.496	1.90321	1.91974
56	273.7	18.1	18.2951	18.009	1.0779	0.50276
58	276.9	26.3	26.0934	26.115	0.78555	0.70342
60	280.7	40.3	40.3699	40.999	0.17345	1.73449
61	283.1	54.3	54.0888	55.125	0.38895	1.51934
50	275.6	19.9	21.4238	21.31	7.65729	7.08543
53	278.5	29.8	29.9992	30.28	0.66846	1.61074
60	280.9	41.4	41.3559	41.98	0.10652	1.40097
59	281.8	44.7	45.6427	46.46	2.10895	3.93736
27	274.6	16.6	16.8361	16.487	1.42229	0.68072
30	276.4	20.8	20.8579	20.639	0.27837	0.77404
32	278.2	25.8	25.786	25.791	0.05426	0.03488
32	280.2	32.8	32.5318	32.881	0.81768	0.24695
33	282	41.2	40.6885	41.511	1.2415	0.75485
21	273.7	14.5	14.8361	14.403	2.31793	0.66897
22	275.9	18.8	19.0524	18.677	1.34255	0.65426
24	277.8	23.7	23.8318	23.613	0.55612	0.36709
25	279.6	29.7	29.5235	29.536	0.59428	0.55219
26	281.6	37.9	37.8304	38.253	0.18364	0.9314
15	282.7	43.7	42.8745	42.931	1.88902	1.75973
				AAD(%)	2.03537	1.97709

Figure 4.7 Methane-Carbon dioxide (CH₄-CO₂) Dissociation Pressure Error vs. Mole Fraction of CH₄ in Gas Phase.

4.3.2.3 CH₄-N₂ Mixed Hydrate

CH₄ as a simple hydrate forms structure I hydrate while N₂ form structure II hydrate, therefore the structure of mixed gas hydrate of CH₄ and N₂ depends on their relative gas composition. The CH₄-N₂ binary gas hydrate undergoes a structure transition from structure I to structure II by the addition of N₂ to the pure CH₄ gas hydrate. The NMR and XRD studies on the mixed hydrate by Lee et al³³ found that the structural change occurs in the range between 0.2524 and 0.2851 mole fraction of CH₄ in gas phase at various temperatures (in the range from 273.3 to 285 K). They also studied the three-phase equilibrium data at different gas compositions and temperature. The phase equilibrium data and the structural transitions are predicted using cell potential method and the three-dimensional phase diagram is given in Figure 4.8. The predictions are tabulated and

compared with CSMGEM and experimental data in Table 4.4. The structural transitions at various temperatures are shown in Figure 4.9 and it is found that the structural transitions occurs in the range between 0.24 and 0.3 mole fraction of CH_4 in gas phase at temperature range from 273 to 282 K which are in agreement with experimental data points³³.

Figure 4.8 The Three-dimensional P - T - y Phase Diagram of Methane-Nitrogen (CH_4 - N_2) Hydrate System.

Table 4.4 Phase Equilibrium Predictions of CH₄-N₂ Hydrate System by This Model and CSMGEM.

%CH ₄	Temperature (K)	Experimental P(Bar)	This Model P(Bar)	CSMGEM P(Bar)	Absolute Error % (This Model)	Absolute Error % (CSMGEM)
87.3	282.8	74	79.107	79.624	6.90135	7.6
87.3	284.6	93.1	96.4662	129.67	3.61568	39.2803
87.3	287.7	145.2	138.644	139.89	4.51529	3.65702
87.3	289.5	171.1	173.638	174.53	1.48346	2.00468
27.2	273.2	79.6	90.9143	71.285	14.2139	10.446
87.3	295.2	313.1	365.355	358	16.6897	14.3405
73.1	273.2	39	35.984	34.29	7.73333	12.0769
50.25	273.2	49.6	52.1477	46.462	5.13649	6.32661
24	273.2	86.2	96.0862	76.826	11.4689	10.8747
10.8	273.2	125.5	125.101	111.36	0.31777	11.2669
84	273.2	36.2	31.3113	30.436	13.5047	15.9227
69	273.2	43.1	38.1412	35.995	11.5053	16.4849
47	273.2	53.5	55.7107	48.901	4.13215	8.59626
35.5	273.2	65.5	73.1086	59.91	11.6162	8.53435
27.5	273.2	77.5	90.4268	70.804	16.6797	8.64
18.5	273.2	106.4	106.613	88.469	0.20056	16.8524
12	273.2	116.5	121.713	107.13	4.47425	8.04292
10	273.2	127.7	127.319	114.35	0.29875	10.4542
65	279.8	71.4	79.6453	106.75	11.548	49.5098
54	279.8	83.7	97.6057	132.85	16.6137	58.7216
25	279.8	155.5	213.816	152.6	37.5021	1.86495
16	279.8	206.7	250.134	192.06	21.0132	7.08273
8.6	279.8	252.3	289.172	239.26	14.6143	5.16845
89.26	273.7	29.9	30.917	30.346	3.40134	1.49164
89.26	274.8	33.1	34.3578	33.892	3.8	2.39275
89.26	275.6	37.3	37.1593	36.741	0.37721	1.49866
89.26	277.1	43.6	43.0446	42.789	1.27385	1.86009
89.26	279.2	52.4	53.0304	53.123	1.20305	1.37977
89.26	281.2	65.8	65.0555	80.875	1.13146	22.9103
89.26	283	81.2	78.838	79.654	2.90887	1.90394
89.26	285.3	101	101.602	103.07	0.59624	2.0495
				AAD (%)	8.07971	11.9108

Figure 4.9 Methane-Nitrogen ($\text{CH}_4\text{-N}_2$) Structural Transitions Predictions. The Curves Represent the Phase Equilibria Predictions at Various Temperatures and Vertical Line Indicate the Structural Transition Boundary.

4.3.2.4 $\text{N}_2\text{-CO}_2$ Mixed Hydrate

As simple gas hydrates CO_2 and N_2 form structure I and structure II respectively. The structure of mixed hydrate can be either structure I or structure II depending on the relative ratio of the two different guest molecules occupied in the small and large cages. The treated flue gases are binary mixtures of CO_2 and N_2 , Kang et al³⁶ developed a hydrate based gas separation process for recovering CO_2 from flue gas using mixed hydrate formation of N_2 and CO_2 . It is important to know the three phase equilibrium conditions of the mixed hydrate $\text{N}_2\text{-CO}_2$ for understanding the separation process. Seo and Lee³⁷ found that the mixed $\text{N}_2\text{-CO}_2$ forms structure I at all

compositions above 0.03 mole fraction of CO₂ in the vapor phase with large cages being occupied by CO₂ and small cages by N₂. The structural changes are predicted for CO₂ and N₂ mixed hydrate in the temperature range of 276-282 K. Figure 4.10 represents the structural changes of mixed hydrates at various temperatures from which it is clear that the structural transition from structure II to structure I occurs at a mole fraction of CO₂ less than 0.1 in gas phase.

Figure 4.10 Nitrogen-carbon dioxide (N₂-CO₂) Structural Transition Predictions. The Curve Represent the Phase Equilibria at Various Temperatures and Vertical Line Represent the Structural Transition Boundary.

The structural transitions are predicted to occur at low concentration of CO₂ in gas phase, which implies that even at low concentration of CO₂ in gas phase the hydrate cages are relatively more occupied by CO₂ resulting in formation of structure I hydrate with high concentration of CO₂ in hydrate phase³⁷. Hence the treated power plant flue gas which contains N₂+CO₂ in the ratio of 80:20 will form structure I. The phase equilibrium calculations are predicted, and the values are

compared with CSMGEM and experimental values in Table 4.5 and Figure 4.11 represents the three-dimensional phase diagram. N_2 dissociation pressures are relatively high when compare to that of the CO_2 , the mixed hydrate forms structure I even at low composition of CO_2 , the peak observed may be due to transition from structure I to structure II and rise in the dissociation pressure.

Figure 4.11 The Three-dimensional P - T - y Phase Diagram of Nitrogen-Carbon dioxide (N_2 - CO_2) Hydrate System.

Table 4.5 Phase Equilibrium Predictions of N₂-CO₂ Hydrate System by This Model and CSMGEM.

%N ₂	Temperature (K)	Experimental P(Bar)	This Model P(Bar)	CSMGEM P(Bar)	Absolute Error % (This Model)	Absolute Error % (CSMGEM)
3.41	274.95	15.65	16.2482	15.971	3.82236	2.05112
3.41	277.45	20.6	21.9336	-	6.47379	-
3.41	280.25	29	31.3144	31.476	7.98069	8.53793
3.41	282.55	40	43.695	44.649	9.2375	11.6225
3.48	273.1	12.2	13.0987	12.815	7.36639	5.04098
3.48	274.6	15.4	15.603	15.324	1.31818	0.49351
3.48	278.3	24.2	24.3857	24.255	0.76736	0.22727
3.48	279.4	28.9	28.0423	28.04	2.96782	2.97578
9.01	280.2	29.5	33.1585	33.83	12.4017	14.678
9.01	273.4	13.7	14.3338	14.164	4.62628	3.38686
9.01	274.1	15.3	15.5613	15.407	1.70784	0.69935
9.01	276.7	18.9	21.2077	21.22	12.2101	12.2751
9.01	279.1	30.9	28.6358	29.023	7.32751	6.07443
14.8	280	36	34.5236	35.862	4.10111	0.38333
15.09	277	26	23.5379	23.927	9.46962	7.97308
17.95	274	17.69	16.9364	17.072	4.26003	3.4935
22.2	274	20	17.7966	18.113	11.017	9.435
22.2	276.15	26	23.0465	23.763	11.3596	8.60385
22.2	280.65	42.25	41.486	44.729	1.80828	5.86746
30.01	280	42.33	41.97	46.571	0.85046	10.0189
40.01	274	23.54	22.6202	24.218	3.90739	2.8802
40.83	280	50.68	49.6072	58.169	2.11681	14.777
43.3	277	33.77	34.4383	38.809	1.97898	14.9215
49.52	274	28.65	26.4828	29.363	7.5644	2.48866
51.85	273.75	31.95	26.84	29.927	15.9937	6.33177
51.85	276	42.57	35.3515	40.779	16.9568	4.20719
51.85	279	58.67	52.6396	64.175	10.2785	9.38299
51.85	281	74.49	71.5063	90.653	4.0055	21.6982
51.85	282	89.75	85.2894	109.86	4.97003	22.4067
60.06	274	35.6	32.8102	37.996	7.83652	6.73034
60.76	280	82.75	75.4198	96.975	8.85825	17.1903
61.01	277	52.33	49.1389	60.13	6.09803	14.9054
74.9	280	149.74	124.871	150.1	16.6083	0.24042
79.43	274	72.35	61.4307	72.775	15.0923	0.58742
82.39	272.85	72.4	59.3311	135.54	18.051	87.2099
82.39	274.05	81.2	72.1435	82.862	11.1533	2.0468

82.39	277	119.8	111.978	124.83	6.52922	4.19866
82.39	277.45	106.5	120.648	133.02	13.284	24.9014
82.91	280	207.53	200.047	194.24	3.60589	6.40389
88.41	274.25	110.2	114.455	110.79	3.86098	0.53539
88.41	275.65	138.7	142.989	132.55	3.092	4.43403
88.41	277.6	181	200.395	170.25	10.7157	5.93923
88.41	278.95	222.3	255.885	202.39	15.1081	8.95637
93.37	277	191.74	214.262	190.85	11.7462	0.46417
95.02	274	149.28	152.014	145.2	1.83146	2.73312
				AAD(%)	7.60705	9.10021

The mole fractions of CO₂ in hydrate phase predicted are plotted against the mole fractions of CO₂ in gas phase for the experimental data points and are found that even at the low concentration of CO₂ in vapor phase the mole fraction of CO₂ in the hydrate is more than 0.5 as shown in Figure 4.12. The points represent the predictions at experimental data points and the lines represent the predictions at 273 K, 277 K and 280 K.

Figure 4.12 Mole fraction of CO₂ in Hydrate Phase vs Vapor Phase for Nitrogen-Carbon dioxide (N₂-CO₂) Mixed Hydrate.

The average absolute deviations (AAD) of the various mixed hydrates predicted by this model and by CSMGEM for the binary hydrates are shown in Figure 4.13. The AAD for CH₄ and C₂H₆ as simple hydrates is 3.5% and 3.85% respectively but for the mixed hydrate it is 9.3%. This may be as simple hydrates both form structure I hydrate, and as mixed hydrate it forms structure II at various gas composition, the reference parameters of both components in structure II have to be verified. Therefore, the correlation found for the reference thermodynamic parameters $\Delta\mu_w^0$ and Δh_w^0 with respect to the size of the guest molecule should be validated by comparing with experimentally-determined reference thermodynamic parameters.

Figure 4.13 Comparison of Average Absolute Deviations from Experimental Data for Mixed Hydrates Predicted by This Model and CSMGEM Software.

4.3.3 Phase Equilibrium of CH₄-N₂-CO₂ Mixed Hydrate

Recent experimental studies by Park et al.⁴¹ have shown that the fraction of recovered methane can be improved to 85% by using a mixture of N₂ and CO₂ when compared with the 64% obtained by pure CO₂. The size of the CO₂ molecule is almost equal to that of the size of small cage of structure I, hence it cannot replace the CH₄ molecule from small cages, it preferentially replaces the CH₄ from the large cages of CH₄ hydrate while N₂ being relatively small molecule, prefers to occupy small cages over large cages it can therefore replace the CH₄ molecules from the small cages of the CH₄ hydrate. The direct use of the N₂+CO₂ mixture could potentially eliminate the CO₂ purification process. Hence, treated power plant flue gases (N₂+CO₂) which forms structure I hydrate can be directly used for replacement process. This could serve the dual purpose of sequestering CO₂ as well as CH₄ recovery from the hydrates and is anticipated to provide required background for developing an economically feasible large-scale process⁴¹ and it also enables the reservoir to be stable even after recovery of CH₄ as it forms same crystalline structure after replacement process. The phase equilibrium conditions of CH₄-N₂-CO₂ hydrate has to be studied in order to understand the replacement process. The phase equilibria of the ternary hydrate are predicted and the predictions await experimental confirmation. Figure 4.14 represents the phase equilibria predictions of the ternary mixture at 274.15 K. Ternary plots of equilibrium gas mixture compositions both in gas and hydrate phase are presented at constant temperature, 274.15 K for varying pressures and at constant pressure, 35 bar for varying temperatures through Figure 4.15 to Figure 4.18. The values 274.15 K and 35 bar are experimental conditions of Park et al.⁴¹. The points on the plots represent the predictions obtained by the cell potential model. At constant temperatures as the pressure increases the phase equilibrium curve shifts upwards but at constant pressure the phase equilibrium curve shifts

upwards with decrease in the temperature which is quite predictable since hydrates are more stable at low temperatures and high pressures.

Figure 4.14 Methane-Nitrogen-Carbon Dioxide ($\text{CH}_4\text{-N}_2\text{-CO}_2$) Phase Equilibria Predictions at 274.15 K.

Figure 4.15 Ternary Plot of Gas Phase Compositions of Methane-Nitrogen-Carbon Dioxide ($\text{CH}_4\text{-N}_2\text{-CO}_2$) Hydrate at 274.15 K.

Figure 4.16 Ternary Plot of Hydrate Phase Compositions of Methane-Nitrogen-Carbon Dioxide ($\text{CH}_4\text{-N}_2\text{-CO}_2$) Hydrate at 274.15 K.

Figure 4.17 Ternary Plot of Gas Phase Compositions of Methane-Nitrogen-Carbon Dioxide ($\text{CH}_4\text{-N}_2\text{-CO}_2$) Hydrate at 35 Bar.

Figure 4.18 Ternary Plot of Hydrate Phase Compositions of Methane-Nitrogen-Carbon Dioxide ($\text{CH}_4\text{-N}_2\text{-CO}_2$) Hydrate at 35 Bar.

4.4 Conclusions

In this work, a correlation between the reference parameters and the guest molecule size was developed. The cell potential code developed by Anderson et al.⁸ is modified for variable reference chemical potential difference and reference enthalpy difference. The model is validated by predicting the experimental structural transitions that are known to occur, such as cyclopropane. The phase equilibria of simple hydrates are predicted and compared with the predictions of CSMGEM¹. The occupancies obtained are more realistic when compared to that of CSMGEM¹ which is verified by the prediction of cage occupancies of CO₂ within the range given by experimental data point given by Ripmeester and Ratcliffe¹⁹. Along with the equilibrium pressure predictions, the ability of this method to predict the occupancies accurately is the rigid test for the reliability of the method.

The cell potential code developed has validated its effectiveness and applicability to mixed hydrate systems by predicting the phase equilibria and structural transitions of the binary hydrates without any adjustable parameters. The three-dimensional (*P-T-y*) phase diagrams are predicted for CH₄-C₂H₆, CH₄-CO₂, CH₄-N₂ and N₂-CO₂ binary hydrates and are compared with the data obtained using CSMGEM¹. Structural transitions of CH₄-C₂H₆, CH₄-N₂ and N₂-CO₂ are calculated using this model and are validated by the experimental structure transition points. The CH₄-CO₂ mixed hydrate phase equilibria is determined in order to understand the replacement process of CH₄ by CO₂ in natural gas hydrates for production of CH₄ from natural gas while sequestering CO₂ simultaneously. The occupancy data of CH₄-CO₂ mixed hydrate obtained by this method have been sent to PNNL and are currently incorporated into STOMP-HYD³² simulator.

The fraction of methane recovered from natural gas hydrates by injecting pure CO₂ was found to be increased by using N₂ + CO₂ binary mixture. In order to understand the replacement process, the phase equilibria of the ternary mixture at 274.15 K is predicted and await the experimental confirmation. Ternary phase diagrams for methane, nitrogen and carbon dioxide at constant temperature for varying dissociation pressures and at constant dissociation pressure for varying temperatures are calculated.

4.5 References

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5 Overall Conclusions and Recommendations

5.1 Conclusions

The overall goal of this thesis was to develop a computationally-tractable model for predicting mixed hydrate phase equilibria that can be implemented into the existing reservoir simulators and to predict the structural transitions that occur in gas hydrates. An empirical correlation of dissociation pressure with respect to temperature and gas phase composition was developed for methane and ethane binary hydrate for structure I and structure II. In the existing statistical thermodynamics model the reference parameters of the empty hydrate lattice are functions of the guest molecule size, therefore a correlation of the reference parameters with the guest size was developed for both structure I and structure II. The cell potential code developed by Anderson et al. was modified for the variable reference chemical potential difference and reference enthalpy difference. The model was validated by reproducing the phase equilibria of simple hydrates. The phase equilibria of the mixed hydrates were predicted without fitting to the experimental data. The structural transitions of the simple hydrates with temperature and in mixed hydrates with respect to their relative gas composition are predicted accurately using this model.

In particular we conclude that:

1. The empirical correlation of dissociation pressure with respect to temperature and gas phase composition for binary gas hydrates was determined and the parameters are determined using linear and non-linear regression analysis.
2. Reference chemical potential difference $\Delta\mu_w^0$ and reference enthalpy difference Δh_w^0 of empty hydrate lattice are function of guest molecule size and an empirical correlation was developed.

3. The predictive ability of the cell potential method was verified against experimental structural transitions that are known to occur. For example, it was predicted that cyclopropane forms structure II in the temperature range 256.4 and 274.6 K which is in agreement with the experimental values 257.1 and 274.6 K.
4. The average absolute deviation of predictions from the experimental data by this method was calculated and compared with CSMGEM. The occupancies obtained from this method are more accurate. For example, CO₂ occupancies are predicted around 20 to 35% in small cages and 98 to 99% in large cages for temperatures ranging 151.5 to 283.3 K which are in agreement with the experimental data point obtained by Ripmeester and Ratcliffe.
5. The cell potential method developed has validated its ability to successfully predict mixed hydrate systems without any adjustable parameters and fitting to the experimental data. The structural transitions in mixed hydrate systems are also predicted accurately.
6. The three-dimensional (P - T - y) phase diagrams are plotted for CH₄-C₂H₆, CH₄-CO₂, CH₄-N₂ and N₂-CO₂ binary hydrates using cell potential method.
7. The structure I to structure II transition for CH₄-C₂H₆ system was predicted to occur at 0.72 mole fraction of CH₄ and it reverts from structure II to structure I at 0.98 mole fraction of CH₄ at 274.2 K within the experimental range calculated to be 0.72-0.75 mole fraction of CH₄ and 0.992($\pm$ 0.005)-0.994($\pm$ 0.007) mole fraction of CH₄.
8. The phase equilibria conditions of CH₄-CO₂ mixed hydrates are studied to understand the replacement process of CH₄ by CO₂. It is observed that most of the large cages are occupied by CO₂ while small cages are occupied by CH₄ molecules.

9. The structure transitions in nitrogen mixed hydrate systems are predicted accurately, N₂-CH₄ are predicted to undergo a structure transition from structure II to structure I at 0.24 and 0.3 mole fraction of CH₄ in the temperature range 273 to 282 K within the experimental data measured to be 0.2524 and 0.2851 mole fraction of CH₄. N₂-CO₂ mixed hydrate, the structural transition from structure II to structure I was predicted to occur at a mole fraction of carbon dioxide in gas phase is less than 0.1.
10. The phase equilibria of ternary mixed hydrate (CH₄-N₂-CO₂) are predicted at 274.15 K and the predictions await experimental confirmation. Ternary plots of equilibrium gas compositions are presented at constant temperature for varying pressures and at constant pressure for varying temperatures.

5.2 Recommendations

1. The correlation found for the reference thermodynamic parameters $\Delta\mu_w^0$ and Δh_w^0 with respect to the size of the guest molecule should be validated by comparing with experimentally-determined reference thermodynamic parameters for some guest molecules calculated by site-site *ab initio* potentials.
2. The Peng-Robinson equation of state was used in this work to model fluid fugacity, it could accurately model fluid fugacity at low pressures; but, at high pressures the Peng-Robinson EOS fails to predict fluid fugacity accurately i.e., it could predict accurately in the L_w-H-V region but fail to predict in L_w-H-L_{hc}. Hence there is a necessity to incorporate a new equation of state into the cell potential code which can model fluid fugacity accurately in wide range of pressures.
3. Natural gas hydrate formed by thermal pyrolysis of fossil organic matter contains methane, ethane and other significant amount of higher hydrocarbons (C₃-C₅). Therefore

there is need to understand the phase equilibria of multi component gas hydrates like methane-ethane- propane, methane-ethane-propane- butane etc.

4. To understand the replacement process of CH_4 from CH_4 hydrate using N_2+CO_2 mixture using this thermodynamic framework and verify with the experimental data published by Park et al. and to implement this to the large scale reservoir grids.
5. To optimize the $\text{N}_2\text{-CO}_2$ ratio using this thermodynamic model, thus predicting the maximum recovery of CH_4 from a natural gas hydrate reservoir while simultaneously sequestering CO_2 .