

DETERMINATION OF WATER CONTENT FOR HYDRATE FORMATION IN GAS-DOMINANT SYSTEMS USING A MULTIPHASE FLASH ALGORITHM

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Dissertação de Mestrado apresentada ao Programa de Pós-graduação em Engenharia Química, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Mestre em Engenharia Química.

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Grant me, Lord, keenness of mind to understand, capacity to retain, method and ease in learning, subtlety in interpreting, grace and abundance in speaking. Grant me, Lord, accuracy in beginning, guidance in progressing, and perfection in concluding. (Saint Thomas Aquinas)

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DETERMINAÇÃO DO CONTEÚDO DE ÁGUA PARA FORMAÇÃO DE HIDRATOS EM SISTEMAS GÁS-DOMINANTE UTILIZANDO UM ALGORITMO DE FLASH MULTIFÁSICO

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Programa: Engenharia Química

Este trabalho aborda os desafios associados à formação de hidratos em sistemas gás-dominante, particularmente na exploração offshore de petróleo e gás. Hidratos, sólidos cristalinos formados sob alta pressão e baixa temperatura, podem bloquear dutos, resultando em riscos operacionais e altos custos de remediação. Para enfrentar esses desafios, o estudo implementa modelos termodinâmicos baseados em mecânica estatística, utilizando a teoria de van der Waals e Platteeuw e equações de estado como PC-SAFT e uma versão modificada de Peng-Robinson. A modelagem é complementada por um algoritmo de flash multifásico e análise de estabilidade permitindo a resolução de equações de balanço de massa e minimização da energia Gibbs total, com restrições de não-negatividade para as frações relativas de cada fase. Essa abordagem permite prever condições de equilíbrio em todo o diagrama de fases, com ênfase em sistemas gás-dominante. Os resultados são comparados com dados experimentais disponíveis na literatura e com simulações do software comercial PVTsim[®]. A pesquisa inclui também a estimação de parâmetros para a PC-SAFT, análise de dados de equilíbrio para sistemas com baixo teor de água e construção de diagramas de fases. Concluiu-se que a equação de estado Peng-Robinson Modificada funciona bem entre 6 bar e 14 bar e a PC-SAFT funciona bem em pressões acima de 20 bar. Os resultados oferecem insights valiosos para prever equilíbrios de hidratos em diferentes condições, tornando operações offshore mais seguras e eficientes, especialmente no pré-sal brasileiro, fornecendo uma ferramenta para prever a formação de hidratos e avaliar a necessidade de mitigação de bloqueios em dutos na indústria de óleo e gás.

Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

DETERMINATION OF WATER CONTENT FOR HYDRATE FORMATION IN GAS-DOMINANT SYSTEMS USING A MULTIPHASE FLASH ALGORITHM

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This work addresses the challenges associated with hydrate formation in gasdominated systems, particularly in offshore oil and gas exploration. Hydrates, crystalline solids formed under high pressure and low temperature, can block pipelines, leading to operational risks and high remediation costs. To tackle these challenges, the study implements thermodynamic models based on statistical mechanics, utilizing the van der Waals and Platteeuw theory and equations of state such as PC-SAFT and a modified version of Peng-Robinson. The modeling is complemented by a multiphase flash algorithm and stability analysis, enabling the resolution of mass balance equations and the minimization of total Gibbs energy, with non-negativity constraints for the relative fractions of each phase. This approach allows for the prediction of equilibrium conditions throughout the phase diagram, with an emphasis on gas-dominated systems. The results are compared with experimental data available in the literature and simulations from the commercial software PVTsim[®]. The research also includes parameter estimation for PC-SAFT, equilibrium data analysis for systems with low water content, and phase diagram construction. It was concluded that the Modified Peng-Robinson equation of state performs well between 6 bar and 14 bar, while PC-SAFT is more accurate at pressures above 20 bar. The results provide valuable *insights* for predicting hydrate equilibria under different conditions, enhancing the safety and efficiency of offshore operations, especially in Brazil's pre-salt region, and offering a tool to predict hydrate formation and assess the need for mitigation measures against pipeline blockages in the oil and gas industry.

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List of Abbreviations

K_{v-s}	Vapor-Solid Equilibrium Constants, p. 11
D_2	Deuterium, p. 5
AARD	Avarage Absolute Relative Deviation, p. 75
ARD	Absolute Relative Deviation, p. 75
CCUS	Carbon, Capture, Utilization and Storage, p. 8
CM	Chilled Mirror, p. 20
CPA-EoS	Cubic Plus Association Equation of State, p. 22
CPA	Cubic Plus Association, p. 22
DFT	Density Functional Theory, p. 91
DSH	Differential Scanning Hygrometer, p. 20
EoS	Equations of State, p. 31
GC	Gas Chromatography, p. 20
GDEM	General Dominant Eigenvalue Method, p. 27
Gasbol	Bolivia-Brazil Gas Pipeline, p. 1
HVE	Hydrate-Vapor Equilibrium, p. 80
HV	Huron-Vidal, p. 22
KF	Karl Fischer, p. 20
KKT	Karush-Kuhn-Tucker, p. 59
LGP	Liquefied Petroleum Gas, p. 1
LNG	Liquefied Natural Gas, p. 1

Mod PR	Modified Peng-Robinson, p. 83
Modified PR	Modified Peng-Robinson, p. 80
NRTL	Non-Random Two-Liquid, p. 21
PC-SAFT	Pertubed Chain Statistical Associating Fluid Theory, p. 9
PR-EoS	Peng-Robinson Equation of State, p. 22
PR	Peng-Robinson, p. 22
PVT	Pressure-Volume-Temperature, p. 31
Psat	Saturation Pressure, p. 73
Psub	Sublimation Pressure, p. 73
QCM	Quartz Crystal Microbalance, p. 20
SRK	Soave-Redlich-Kwong, p. 22
TDLAS	Tunable Diode Laser Absorption Spectroscopy, p. 20
THF	Tetrahydrofuran, p. 4
TPDF	Tangent Plane Distance Function, p. 27
UML	Unified Modeling Language, p. 63
tPC-SAFT	truncated Perturbed Chain-Statistical Associating Fluid Theory, p. 91
vdWP	van der Waals and Platteeuw, p. 14

Chapter 1

Introduction

1.1 Natural Gas

Natural gas is one of the main fossil fuels used in the world today, playing an essential role in the global energy sector. Composed primarily of methane (CH_4) , it can be found both in independent reservoirs and associated with oil deposits, being widely used in electricity generation, heating, industry, and as a raw material for chemical products. Its importance stands out due to its high energy efficiency and lower environmental impact compared to coal and oil, as its combustion emits less carbon dioxide (CO_2) and releases virtually no sulfur, reducing air pollution. Additionally, it is a strategic resource for the energy security of many countries and can be transported through pipelines or in liquefied form (LNG), facilitating its global trade[14].

The gas industry in Brazil began in the 19th century with the production of gas from coal for public lighting. In the 20th century, LPG (liquefied petroleum gas) became the primary domestic fuel. The introduction of natural gas into the Brazilian energy matrix gained momentum in the 1990s, with the discovery of reserves and the construction of the Bolivia-Brazil Gas Pipeline (Gasbol) in 1999, enabling the import of Bolivian gas and fostering the expansion of the domestic market. The National Energy Plan (PNE 2030) projects that natural gas will account for 15 % of Brazil's energy matrix by 2030, with an average annual growth rate of 6.1 %, surpassing the global average [15].

1.2 Natural Gas Hydrates

Hydrates are crystalline solids formed by water molecules that interact with each other through hydrogen bonding (host), forming cavities that are occupied by small molecules present in natural gas (guest), thereby stabilizing the structure (Figure 1.1). The interaction between the crystalline network and the guest molecule occurs through van der Waals forces, without any chemical bonding between them [16]. These solids form at low temperatures and/or high pressures, typical of offshore deep-water exploration fields. This process of trapping a molecule or atom within a cage-like structure, such as gas hydrates (clathrates), is called enclathration [17] [18] [19].



Figure 1.1: Enclathration of a Molecule Present in Natural Gas.

Figure created by the author, inspired by the graphical representation of VAS-CONCELOS(2021).

Research on natural gas hydrates began in the 1930s, when Hammerschmidt discovered that they could block pipelines even at temperatures above the freezing point, leading to regulations on water content in natural gas and the start of modern investigations. Prior to 1934, researchers such as Villard and de Forcrand studied their compositions and properties. In 1895, Villard proposed Villard's Rule, according to which hydrates crystallized regularly with the formula $M + 6H_2O$. This rule was based on the concept of stoichiometric inorganic hydrates with fixed ratios. However, later research showed that clathrate hydrates are non-stoichiometric, with variable and flexible compositions, better described by thermodynamic models, such as that of VAN DER WAALS and PLATTEEUW (1959).

During World War II, Deaton and Frost conducted detailed experiments on hydrate formation from pure components and mixtures, although limitations in composition measurements were recognized. These studies also evaluated inhibitors such as methanol and monoethylene glycol. Between 1959 and 1967, Jeffrey and collaborators analyzed the crystalline structures of clathrate hydrates, confirming their classification as compounds that trap guest molecules in cages formed by water molecules. Von Stackelberg contributed to the classification of hydrates into types such as simple (single guest), mixed, double, hilfgase (auxiliary gas), highlighting their specific compositions and functions. These discoveries laid the foundations for the modern understanding of hydrates, their crystalline structures, and their impact on the natural gas industry.

These solids can occur in three structural types, referred to in the literature as sI, sII, and sH [21]. The structures of natural gas hydrates differ primarily in the size and shape of the water cages that trap gas molecules (guests) and the size of the gas molecules that can be accommodated. These differences are determined by the geometry of the cages formed by hydrogen bonds between water molecules (Figure 1.2).



Figure 1.2: Structures of the Crystalline Solid.

Figure created by the author, inspired by the graphical representation of ZOU (2013).

The Structure I (sI) of gas hydrates consists of two cage configurations: a small

one, called 5^{12} , which has a pentagonal dodecahedron shape with 12 pentagonal faces, and a larger one, called $5^{12}6^2$, which has a tetrakaidecahedron shape with 12 pentagonal faces and 2 hexagonal faces. Each unit cell contains 2 small cages and 6 large ones. This structure accommodates small guest molecules with diameters between 0.48 and 0.60 nm, with the most common examples being methane (CH₄) and ethane (C₂H₆). Structure I is predominant in natural environments, especially in oceanic sediments and permafrost regions.

The Structure II (sII) of gas hydrates features small cages of the 5^{12} type, identical to those in Structure I, and large cages of the $5^{12}6^4$ type, with a hexakaidecahedron shape containing 12 pentagonal faces and 4 hexagonal faces. Each unit cell is composed of 16 small cages and 8 large ones. This structure accommodates moderately sized guest molecules, with diameters ranging from 0.60 to 0.90 nm. Common examples of gases forming this structure include propane (C₃H₈) and isobutane (C₄H₁₀), which can also be combined with smaller molecules, such as methane and ethane. Structure II is more frequently found under industrial conditions and in hydrocarbon mixtures.

The Structure H (sH) of gas hydrates contains cages of different sizes, including small ones of the 5^{12} type, identical to those in Structure I, medium ones of the $4^35^66^3$ type, with an irregular dodecahedron shape, and large ones of the $5^{12}6^8$ type, which have an icosahedron shape with 12 pentagonal faces and 8 hexagonal faces. Each unit cell contains 3 small cages, 2 medium cages, and 1 large cage. This structure can accommodate large guest molecules with diameters exceeding 0.90 nm. Common examples of gases forming this structure include compounds such as neopentane and cyclopentane, as long as they are stabilized by methane or other smaller gases. Structure H is rarer and typically found in complex mixtures of heavy hydrocarbons.

Clathrate hydrates exhibit different types of cage occupancy depending on the type of guest molecule, pressure, and temperature. SLOAN and KOH (2008) classifies these occupancies based on a historical nomenclature, as discussed below:

- 1. Stoichiometric Occupancy: It is assumed that each cage contains a single guest molecule, maintaining a fixed (stoichiometric) ratio between water molecules and guests.
- 2. Non-Stoichiometric (Partial Occupancy): Some cages may remain empty or contain fewer molecules than expected, depending on the solution composition, pressure, and temperature.
- 3. Multiple Occupancy (High Pressure): At elevated pressures, it is possible for more than one guest molecule to occupy the same cage. This property is

mainly observed under extremely high pressures, enabling the formation of dense and stable hydrates.

- 4. **Promoter-Stabilized Occupancy**: Promoter molecules, such as tetrahydrofuran (THF), can stabilize hydrates at lower pressures by filling large cavities and facilitating the occupation of small cages by other molecules.
- 5. Occupancy Variation with Pressure and Temperature: The occupancy of cages can dynamically change as a function of environmental conditions. In the case of D_2 (deuterium), the occupancy of large cages varies from two to four molecules per cage, depending on temperature.

1.3 Gas-Dominant System

The three types of systems in multiphase flows used to study hydrate formation in oil and gas transportation lines are the oil-dominant system, the water-dominant system, and the gas-dominant system [22] [23]. The oil-dominant system is primarily composed of oil, with small amounts of gas and water, where water can be emulsified in oil or vice versa, forming dispersed droplets. In this case, hydrate formation predominantly occurs at the interfaces between oil and water. The waterdominant system has water as the predominant phase, accounting for more than 70 % by volume, with gas present as dispersed bubbles in the water. In this system, hydrates primarily form at the interface between gas and water. Meanwhile, the gas-dominant system is composed mainly of gas, with small quantities of liquid hydrocarbons and/or water. These systems are illustrated in Figure 1.3, highlighting the differences in composition and hydrate formation patterns for each case.



Figure 1.3: Types of Hydrate Formation Systems.

Figure created by the author, inspired by the graphical representation of DEX-TRE (2017).

Gas-dominant systems pose significant challenges in the oil and gas industry due to hydrate formation, which can cause blockages in transportation lines, leading to operational risks and high remediation costs. These systems operate under highpressure and low-temperature conditions, which favor the formation of hydrates. Formation occurs in liquid droplets suspended in the gas or at the gas-liquid interface and is strongly influenced by factors such as gas velocity and the degree of subcooling. Small amounts of liquids present can act as sources for nucleation and hydrate growth at gas-liquid interfaces. Hydrates may grow on the internal walls of pipelines or within suspended droplets, forming solid deposits known as "stenosis", whose continuous deposition reduces the hydraulic diameter and can increase pressure losses in the system, potentially leading to total blockages in extreme cases [24].

Figure 1.4 shows the behavior of the phase envelope as the water content decreases. In gas systems in equilibrium with an aqueous phase, known as free water, the fugacity of water primarily depends on temperature, as water is nearly pure. In contrast, in gas-dominated systems, all the water is dissolved in the vapor phase. In this case, the fugacity of water is approximately proportional to its partial pressure, exhibiting behavior similar to that of an ideal gas [12]. This reduces water's tendency to form a new phase, requiring the fugacity in the new phase to be lower. Thus, the lower the water content in the vapor phase, the lower the temperature and/or higher the pressure required for hydrate formation, shifting the equilibrium curve to more extreme conditions. In systems composed of hydrate-forming components in the gas phase (Gas Dominated), with low water content dissolved in the gas, regions of ice precipitation (I+V) are observed with decreasing temperature at low pressure, and regions of hydrate precipitation (H+V) are observed with decreasing temperature at low pressure at high pressure or with increasing pressure.



Temperature

Figure 1.4: Illustration of the Equilibrium Curve Behavior With Decreasing Water Content.

Figure created by the author, inspired by the graphical representation of SEG-TOVICH (2014).

1.4 Motivation

Gas-dominated systems are understudied and pose significant risks, often causing complete pipeline blockages, representing a major operational challenge in natural gas transportation pipelines. Particularly in offshore production regions, such as the Brazilian Pre-Salt fields, the high-pressure and low-temperature conditions present in deep waters make these systems highly susceptible to hydrate formation, which can block pipelines and disrupt production and transportation operations. Figure 1.5 illustrates the path taken by the extracted gas from the well to the seabed. The gas inside the well is at high pressure and temperature. Upon reaching the seabed, a cold region, it undergoes an abrupt drop in temperature and pressure, causing the flow in this section to enter the phase envelope region where hydrate formation occurs.



Temperature

Figure 1.5: Illustration of Temperature and Pressure Variation Along the Production Line.

Figure created by the author, inspired by the graphical representation of SLOAN and KOH (2008).

In Brazil, the relevance of studying gas hydrate formation is heightened due to the significant presence of carbon dioxide in Pre-Salt fields, where concentrations can reach up to 80%. This characteristic substantially increases the risk of hydrate formation, requiring the development of robust prediction and control methods [25]. Furthermore, with the advancement of global strategies for reducing carbon emissions, carbon capture, utilization, and storage (CCUS) has become a promising alternative to mitigate the environmental impacts associated with oil and gas production.

However, the implementation of CCUS presents significant operational challenges, particularly concerning the transportation and storage of CO_2 -rich streams. Among these challenges, gas hydrate formation stands out as one of the main obstacles, as these crystalline solids can obstruct pipelines, reduce process efficiency, and compromise operational safety. Additionally, the presence of impurities such as N_2 , O_2 , H_2 , CO, H_2S , and SO_2 in CO_2 -rich mixtures can significantly alter hydrate formation behavior, impacting equilibrium conditions and the reliability of thermodynamic predictions. Even at very low concentrations, moisture content can be sufficient to induce hydrate formation under typical operational conditions for CO_2 transport and injection.

Given this scenario, it is essential to understand the mechanisms of hydrate formation and deposition in gas-dominated systems. While previous efforts have mainly focused on oil-dominated systems, gas flows require new approaches due to differences in flow regimes, such as stratified and annular flows.

Therefore, in the Brazilian context, where production occurs in ultra-deep waters and the extracted natural gas has unique characteristics, a detailed study of gasdominated systems is crucial to ensuring the safety and efficiency of operations. The implementation of more accurate predictive models and effective control strategies will help minimize operational risks and enable the safe transportation and storage of CO_2 , aligning with energy transition and sustainability guidelines.

Moreover, most experimental data used to validate models are limited to specific conditions of temperature, pressure, and composition. Data covering complex mixtures or extreme conditions, such as those found in Pre-Salt fields, are scarce, reducing the reliability of predictions in more challenging systems [25].

1.5 Objective

Study the formation of hydrates in gas-dominated systems using a multiphase flash calculation algorithm and phase stability analysis.

1.5.1 Steps

- Compile a dataset from the literature on hydrate-vapor equilibrium and identify existing gaps;
- Implement the multiphase flash calculation algorithm and phase stability analysis, along with thermodynamic models, computationally;
- Estimate some parameters of the PC-SAFT (Pertubed Chain Statistical Associating Fluid Theory) equation of state for pure components, like pure components parameters and cross-association parameter of water;
- Determine the accuracy of the models in calculating the water content in gas for gas-dominated systems in equilibrium with hydrate;

• Compare the simulations obtained with the implemented models to those produced using the PVTsim[®] software.

1.6 Dissertation Outline

The dissertation is divided into five chapters, with the references provided after the final chapter.

Chapter 1 introduces the study by contextualizing natural gas, highlighting the importance of hydrates in gas-dominated systems, and addressing associated industrial challenges. Chapter 2 presents a literature review and the theoretical background, covering hydrate formation prediction methods, hydrate equilibrium in gas dominant systems, multiphase flash calculation methods, stability analysis and tangent plane distance, and computational tools such as the PVTsim[®] software.

Chapter 3 details the modeling of fluid phases, ice, and hydrate, describing the equations of state used, the multiphase flash algorithm with stability analysis, as well as the computational implementation. Chapter 4 discusses the results, reviews equilibrium data for systems with low water content, estimates parameters for the PC-SAFT model, and presents equilibrium simulations for gas-dominated systems, comparing them to experimental data and PVTsim[®] results, followed by a discussion on phase diagrams.

Finally, Chapter 5 provides the conclusions and suggestions for future work, summarizing the study's scientific contributions, identifying its limitations, and proposing directions for continued research.

Chapter 2

Theoretical Background

2.1 Hydrate Formation Prediction Methods

This section presents the hydrate formation prediction models developed over the years and available in the literature. The hydrate formation prediction method described by WILCOX et al. (1941) and CARSON and KATZ (1941) is based on experimental data and an analogy with vapor-liquid equilibria to model vapor-solid equilibria in hydrate formation, using vapor-solid distribution coefficient (K_{v-s}) . This method is also based on vapor-solid phase equilibrium, using the vapor-solid distribution coefficient—the ratio of the mole fraction of a component in the vapor phase to its mole fraction in the solid phase—to describe the relationship between the concentrations of gaseous components in the solid and vapor phases. It relies on the analogy between vapor-liquid and vapor-solid equilibria to predict hydrate formation in multicomponent natural gas systems. This method assumes that hydrates form solid solutions with variable compositions depending on pressure and temperature, analogous to the behavior of phases in vapor-liquid equilibrium. Hydrate formation conditions can then be determined using dew point calculations. It is complemented by pressure-temperature graphs derived from experimental data for different natural gas compositions, covering specific gravities ranging from 0.6 to 1.0.

KATZ (1945) combined thermodynamic fundamentals with experimental data to predict the pressure and temperature conditions under which hydrates may form. He utilized the specific gravity method, which is a simple and practical approach for predicting hydrate formation conditions in natural gas mixtures, based on the relationship between temperature, pressure, and the specific gravity of the gas. Specific gravity is defined as the ratio of the molecular weight of the gas to that of air, and this property is used as a central parameter in graphs developed by Katz to estimate hydrate formation points under three-phase conditions (liquid water, hydrate, and vapor). The method allows calculating the gas specific gravity and, from it, directly determining the unknown variable, whether pressure or temperature, for hydrate formation directly using the graph. It was initially designed to predict hydrate formation limits during adiabatic expansions, such as throttling in valves, and is particularly useful as a preliminary tool due to its ease of application. While it is a quick and useful method for initial analyses, its accuracy is limited because it was developed based on restricted experimental data and approximate calculations using vapor-solid equilibrium constants (K_{v-s}) . Furthermore, the method is more suitable for hydrocarbon-based gases and may show significant deviations when applied to mixtures with non-combustible components such as CO_2 , $H_2S \in N_2$.

Between the 1940s and 1950s, von Stackelberg and collaborators summarized decades of X-ray diffraction experiments, whose interpretation enabled the determination of two hydrate structures, sI and sII [17].

VAN DER WAALS and PLATTEEUW (1959) explored the formation and thermodynamic behavior of clathrate compounds, with an emphasis on systems containing hydroquinone and gas hydrates. The authors describe these compounds as solid solutions in which gas molecules are trapped within cavities formed by stable structural networks of host molecules, maintained by hydrogen bonds. The stability of these structures is attributed to weak interactions between the trapped components and the host matrix. Although clathrates exhibit solid-like properties, they are analyzed as thermodynamic solutions.

The statistical theory developed by VAN DER WAALS and PLATTEEUW (1959) is based on the general partition function, accounting for various cavities and types of trapped molecules. The formulation of the theory uses the localized ideal adsorption model approach and generalizes the Langmuir isotherm, expressed as Eq. 2.1.

$$y_{ki} = \frac{C_{ki}P_k}{1 + \sum_j C_{ji}P_j}$$
(2.1)

Here, y_{k_i} is the probability of finding a molecule k in a cavity of type i, C_{ki} is the constant associated with the interaction between molecule k and the cavity, and P_k is the partial pressure or fugacity of k. The analysis of thermodynamic equilibrium is described by the equality of chemical potential between the solid and gaseous phases (Eq. 2.2).

$$\mu_Q - \mu_Q^0 = kT \sum_i v_i \ln\left(1 - \sum_k y_{ki}\right) \tag{2.2}$$

Here, μ_Q is the chemical potential of the solvent (host) and ν_i is the fraction of cavities of type *i*. The authors apply these formulations to describe clathrates with a single type of cavity, such as hydroquinone clathrates, and systems with multiple

cavities, such as gas hydrates (structures I and II). The calculations highlight the influence of the size of the trapped molecules and pressure on clathrate stability. The analysis also includes the application of the Lennard-Jones and Devonshire method to determine cellular partition functions and the energetic properties of the system.

MCKOY and SINANOĞLU (1963) introduced innovations to the van der Waals and Platteuw model by considering more realistic intermolecular potentials to describe the interactions between molecules confined in gas hydrate cavities. While van der Waals and Platteuw used the Lennard-Jones (12-6) potential, which treats interactions in a simplified and isotropic manner, McKoy and Sinanoğlu proposed the use of the Kihara potential expressed by Eq. 2.3, which includes a hard core to better represent the size and shape of guest molecules. This approach led to significant improvements in predicting dissociation pressures for non-spherical molecules such as CO_2 and C_2H_6 , reducing discrepancies between theoretical and experimental results.

$$\Phi(p) = \varepsilon \left[\left(\frac{p_m}{p} \right)^{12} - 2 \left(\frac{p_m}{p} \right)^6 \right]$$
(2.3)

Here, p_m is the minimum distance between the nuclei of the molecules, and ϵ is the depth of the potential well.

CHILD (1964) brought another important innovation to the van der Waals and Platteuw model by explicitly considering the effect of cavity size and shape on the thermodynamic and structural behavior of clathrates. While the van der Waals and Platteuw model assumed spherical and uniform cavities, Child investigated how different cavity sizes impact the potential energy and stability of clathrates, analyzing three cases: cavities much larger than the guest molecules, resulting in near-zero internal energies due to the predominance of attractive forces; slightly larger cavities, where guest-host interactions are dominated by moderate dispersion and repulsion forces; and slightly smaller cavities, where repulsive forces become dominant, reducing structural stability. Another significant contribution by Child was the explicit inclusion of configurational entropy (\bar{S}_c) as part of the expression for the entropy change during dissociation as in Eq. 2.4.

$$\Delta \bar{S} = R \ln \left(\frac{\bar{V}}{\bar{V}_f}\right) - R + \bar{S}_c \tag{2.4}$$

Here, \overline{V} is the molar volume of the guest in the standard state, and \overline{V}_f represents the "free" volume available in the cavity. This approach allowed for a better modeling of combinatorial effects resulting from the partial occupancy of cavities, something that the van der Waals and Platteuw model did not directly address.

SAITO et al. (1964) made significant advances in the thermodynamic modeling

of gas hydrates at high pressures, utilizing the van der Waals and Platteuw solid solution theory combined with statistical mechanics and classical thermodynamic principles. He proposed a detailed approach to predict the thermodynamic equilibrium of systems containing hydrates, gas, and water-rich liquid above and below the ice-hydrate-liquid-gas (I+H+L+G) quadruple point. The article also developed a methodology to calculate the chemical potential of water in the hydrate (μ_w) and the chemical potential difference between the hydrate and liquid ($\Delta\mu$) as a function of pressure and temperature, as shown in Eq. 2.5, including experimental adjustments for gases such as methane, argon, and nitrogen. The Clapeyron equation was applied to integrate dependencies between enthalpy ($\Delta \bar{H}$) and molar volume ($\Delta \bar{V}$) with pressure-temperature equilibria, providing a robust model to describe system behavior under extreme conditions. For equilibrium between the hydrate, water-rich liquid, and gas, the chemical potential of water in the hydrate equals that of water in the water-rich liquid (Eq. 2.6).

$$\frac{\Delta\mu}{RT} = -\int \frac{\Delta\bar{H}}{RT^2} dT + \int \frac{\Delta\bar{V}}{RT} \frac{dP}{dT} dT$$
(2.5)

$$\mu_w^{PW} = \mu_w^{Aq} - RT \ln x_w^{Aq} \tag{2.6}$$

PARRISH and PRAUSNITZ (1972) provide a detailed parameterization of experimental data for 15 hydrate-forming gases, enabling accurate predictions of dissociation pressures in multicomponent systems. This extension of the theory to gas mixtures addresses the limitations of empirical methods, such as K-factor charts, ensuring robust and reliable predictions with deviations below 2 °C.

HOLDER et al. (1988) innovates by using empirical correlations, such as the Q^* factor, to adjust predictions for non-spherical molecules in the calculation of the Langmuir constant (C) as Eq. 2.7. The Q^* and C^* factors are expressed by Eq. 2.8 and Eq.2.9, respectively.

$$C = C^* Q^* \tag{2.7}$$

$$C^* = \frac{4\pi}{kT} \int_0^R \exp\left(-\frac{W_1(r) + W_2(r) + W_3(r)}{kT}\right) r^2 dr$$
(2.8)

$$Q^* = \exp\left(-a_0 \left[\frac{\sigma}{R-a}\right]^n\right) \tag{2.9}$$

KLAUDA and SANDLER (2000) introduced significant advancements compared to the traditional van der Waals and Platteeuw (vdWP) models. The innovations of the model include the elimination of the need for reference energy parameters, which are typically used in vdWP models. Furthermore, this work abandons the assumption that the hydrate crystal structure remains constant, a notion that contradicts quantum chemistry calculations. To achieve this, it employs published Kihara cell potential parameters obtained from viscosity and second virial coefficient data, instead of fitting these parameters to hydrate data. A methodological highlight was the use of quantum calculations to reduce the number of adjustable parameters. The model proposes equations for the molar volume of hydrate structures I and II, accounting for variations with temperature and pressure, as shown in Eq. 2.10 and Eq. 2.11.

$$\bar{V}_{w}^{\beta}, I(T, P) = \left(11.835 + 2.217 \times 10^{-5}T + 2.242 \times 10^{-6}T^{2}\right) \times 10^{-30} N_{A} N_{w}^{\beta} -8.006 \times 10^{-9}P + 5.448 \times 10^{-12}P^{2}$$
(2.10)

$$\bar{V}_{w}^{\beta}, II(T, P) = (17.13 + 2.249 \times 10^{-4}T + 2.013 \times 10^{-6}T^{2} + 1.009 \times 10^{-9}T^{3}) \times 10^{-30}$$
$$N_{A}N_{w}^{\beta} - 8.006 \times 10^{-9}P + 5.448 \times 10^{-12}P^{2}$$
$$(2.11)$$

BAZANT and TROUT (2001) introduced an analytical method to extract intermolecular potentials directly from experimental Langmuir constant data for clathrate hydrates. This approach eliminates the need for empirical numerical adjustments, such as those based on the Kihara potential, and allows for the determination of average spherical potentials in a simpler and more interpretable manner. The central innovation lies in the exact inversion of the non-linear integral equation 2.12.

$$C(\beta) = 4\pi\beta \int_0^\infty e^{-\beta w(r)} r^2 dr \qquad (2.12)$$

Let $C(\beta)$ represent the Langmuir constant, $\beta = 1/kT$ the inverse of temperature, and w(r) the average spherical cell potential. This methodology is applied to ethane and cyclopropane hydrates, resulting in analytical solutions and revealing significant limitations of previous methods, such as the high sensitivity of Langmuir constant fitting to variations in the cell potential. Additionally, the authors explore asymptotic behaviors and analyze how non-central potentials can be modeled, offering a new perspective on intermolecular forces in hydrate systems.

BALLARD and SLOAN (2002) proposed a new direct derivation for the standard-state fugacity of the empty hydrate lattice, allowing for the description of the hydrate state itself rather than focusing solely on specific phase transitions. Furthermore, they eliminate the traditional assumption that hydrates behave as ideal solid solutions, introducing structural activity coefficients that account for non-ideal interactions between components. Spectroscopic data are also incorporated directly into the model to optimize parameters, enhancing the accuracy of hydrate descriptions. Another significant innovation is the consideration of volume dependence, introducing a function that relates the hydrate cavity radio to the lattice parameter, accounting for lattice distortions due to guest composition. The authors further propose a multi-layer model to better describe interactions between guests and water molecules within the cavities, based on direct X-ray diffraction data.

Additionally, BALLARD and SLOAN (2002) proposed model can predict hydrate equilibrium with various phases (such as solid-vapor and liquid-vapor), significantly expanding the limitations of previous models. This article is the first in a series of four, collectively aiming to create a comprehensive model for hydrate prediction, including its integration into multiphase routines. Finally, preliminary predictions using the model demonstrate greater applicability, such as accurately describing behavior at high pressures and predicting the maximum formation temperature for type I hydrates. The fundamental equations used in the article include, for instance, the expression for water activity in the hydrate, given by Eq. 2.13.

$$a_{w,H} = \gamma_{w,H} \prod_{m} \left(1 - \sum_{j} \theta_{jm} \right)^{\nu_{m}}$$
(2.13)

Let $\gamma_{w,H}$ represent the activity coefficient of water in the hydrate, θ_{jm} the fractional occupancy of guest j in cavity m, and ν_m éthe number of cavities per water molecule. Another important equation is the expression for the chemical potential of water in the hydrate, considering non-ideal contributions, as shown in equation 2.14.

$$\mu_{w,H} = g_{w,\beta} + RT \sum_{m} \nu_m \ln\left(1 - \sum_{j} \theta_{jm}\right) + RT \ln \gamma_{w,H}$$
(2.14)

Let $g_{w,\beta}$ represent the Gibbs energy of water in the standard lattice of the empty hydrate and RT the product of the universal gas constant and temperature. These innovations make the model more robust and applicable to a wide range of thermodynamic conditions and compositions, overcoming the limitations of traditional methods.

KLAUDA and SANDLER (2003) highlighted the double occupancy of cavities in nitrogen hydrates at high pressures, a phenomenon not predicted by the vdWP model. This phenomenon occurs when two smaller molecules share the same cavity in a hydrate, specifically the large cavities $(5^{12}6^4)$ present in the crystalline sII structure. Double occupancy is relevant at high pressures and elevated temperatures above 300 K, where traditional models, such as the van der Waals and Platteeuw (vdWP) model, fail to accurately predict hydrate equilibrium pressures. The fugacity-based model proposed by the authors incorporates this consideration by reformulating the equation for the chemical potential of the hydrate phase, including a term for double occupancy (Eq. 2.15).

$$\Delta \mu_w^H(T, P) = RT \sum_m \nu_m \ln \left(1 + \sum_j C_{mj} f_j + C_{ml}^{(2)} f_l^2 \right)$$
(2.15)

Let $C_{ml}^{(2)}$ represent the Langmuir constant for double occupancy, which includes interactions between the two guests in the same cavity and between each guest and the water lattice. The authors observed that, in nitrogen hydrates, double occupancy becomes significant at high pressures due to the small size of the nitrogen molecule and the high thermal stability of the sII structure. The interactions between the two nitrogen molecules in the cavity $(w_{g_1-g_2})$ were modeled using accurate interaction potentials, such as the Etters potential, which describes the solid and fluid phases of nitrogen. These calculations demonstrated that double occupancy significantly improves model predictions, reducing deviations in equilibrium pressures. Without considering double occupancy, both the fugacity model and the vdWP model underestimate equilibrium pressures at high temperatures and pressures for nitrogen hydrates. However, with the inclusion of this effect, the fugacity model more accurately predicts hydrate formation under extreme conditions, which is crucial for industrial applications and the study of hydrates in natural environments, such as the ocean floor or permafrost regions. Therefore, considering double occupancy not only enhances the accuracy of equilibrium calculations but also highlights the complexity of hydrate formation mechanisms and how they can vary with composition and thermodynamic conditions.

BANDYOPADHYAY and KLAUDA (2011) present an updated thermodynamic model for gas hydrate formation and stability predictions, utilizing the PSRK equation of state. The primary distinction of this approach lies in using host-guest interactions based on quantum mechanics rather than fitting to experimental data, which provides the model with greater predictive capability. Additionally, the calculation of the Langmuir constant (Eq. 2.16), which measures cavity occupancy by gases, is performed through an empirical correlation, integrating parameters adjusted from theoretical and experimental data. The model also incorporates lattice distortion effects and can handle electrolytes and hydrate formation inhibitors.

$$\ln[C_m(T)] = A_C + \frac{B_C}{T} + \frac{D_C}{T^2}$$
(2.16)

HSIEH <u>et al.</u> (2012) utilized a pressure- and temperature-dependent square-well potential for the Langmuir constant (Eq. 2.17), which accounts for the reduction

in the free volume available to encapsulated gas molecules as pressure increases. This represents an advancement over previous models that treated free volume as constant.

$$C_{ml} = \frac{4\pi}{kT} V_{ml} \exp\left(\frac{\varepsilon_{ml}}{kT}\right) \tag{2.17}$$

Let V_{ml} represent the free volume of gas molecule l within a cavity of type m, and ϵ_{ml} the depth of the square-well potential.

SEGTOVICH et al. (2022) incorporates lattice compressibility and cavity distortion, factors neglected in previous models. This model introduces a natural pressure offset between the hydrate and the isochoric reference empty lattice, reflecting the differences in lattice volume for various guest species under the same thermodynamic conditions. Additionally, the model derives thermodynamically consistent expressions for properties such as chemical potential and molar volume, addressing inconsistencies observed in phase equilibrium calculations of earlier models. The authors propose an iterative algorithm to calculate the pressure offset (ΔP) between the empty lattice and the filled hydrate, considering the interdependence between cavity occupancy, cavity radii, and the molar volume of the lattice. The fundamental equations include: a) the relationship between pressure and chemical potential (Eq. 2.18), b) calculation of the pressure offset, c) the geometric relationship between cavity ratio (R_j) (Eq. 2.19), and d) the molar volume of the lattice (V^{EL}) (Eq. 2.20).

$$P = -\frac{\partial \Psi}{\partial V_H} \tag{2.18}$$

$$\Delta P_{H-EL} = RT\left(\sum_{j} \nu_{j} \sum_{i} \frac{\Theta_{ij}}{C_{ij}} \left(\frac{\partial C_{ij}}{\partial V_{EL}}\right)\right)$$
(2.19)

$$R_j = R_{j,0} \left(\frac{a_{uc}}{a_{uc,0}}\right)^{k_{R_j}/k} \tag{2.20}$$

The model was applied to predict the behavior of methane, ethane, and xenon hydrates, demonstrating good agreement with experimental data under three-phase equilibrium conditions and variations in lattice size. It also overcomes the limitations of inconsistent models, ensuring the validity of the Clapeyron equation at high pressures. This approach is particularly relevant for industrial scenarios, such as natural gas production from hydrates at great depths, where compressibility and host-guest interactions are critical.

The literature review highlights the significant evolution in the modeling and prediction of gas hydrate formation, from early methods based on experimental data and analogies with vapor-liquid equilibria, such as Katz charts, to modern approaches grounded in statistical mechanics, advanced thermodynamics, and quantum mechanics. Early methods played a crucial role in establishing a basic understanding of hydrate formation phenomena but exhibited limitations in accuracy and scope.

The introduction of thermodynamic models, such as the van der Waals and Platteeuw (vdWP) model, marked a significant breakthrough by enabling a more rigorous description of multiphase systems. Subsequently, innovations such as the incorporation of more realistic intermolecular potentials, adjustments for double occupancy, and the consideration of lattice distortion provided substantial improvements, particularly under extreme pressure and temperature conditions.

Despite these advances, challenges remain, such as the need for better integration of non-ideal host-guest interactions and lattice compressibility. The practical importance of these models is evident in industrial applications, such as natural gas transportation and processing. In the present work, it was considered that the crystalline lattice undergoes distortion, using a lattice volume model as a function of temperature and pressure, as presented in Chapter 3.

2.2 Hydrate Equilibrium in Gas Dominant Systems

Given the scarcity of experimental data on hydrate-vapor equilibrium and the challenges faced by thermodynamic models in predicting water content in gasdominated systems, a detailed overview is presented on the limitations of existing experimental studies. This includes challenges in measuring gas humidity, variations in equilibrium conditions, and the performance of major thermodynamic approaches, evaluating both cubic and associative equations of state in predicting water solubility in equilibrium with hydrates. Additionally, the need for new experimental data and improvements in predictive models is highlighted, aiming at industrial applications such as natural gas transportation and CO_2 capture. This review underscores the importance of continuing experimental investigations and optimizing thermodynamic modeling to enhance the understanding of hydrate-vapor equilibrium behavior in gas-dominated systems.

The water content in the gas phase in equilibrium with hydrates (hydrate-vapor equilibrium) is a key parameter for predicting hydrate formation and dissociation in gas-dominated systems. However, the limited availability of experimental data in the literature has been emphasized by various authors, who highlight methodological difficulties and significant variations among the few available studies, complicating the calibration and validation of thermodynamic models [38][39][40]. Obtaining precise measurements of this equilibrium is challenging due to the low solubility of water in gas and the requirement for highly sensitive techniques for quantification at ppm levels [6]. Subsequent studies, such as those by CHAPOY et al. (2003), YOUSSEF <u>et al.</u> (2009), and ZHANG <u>et al.</u> (2011), identified significant discrepancies in reported data, suggesting that water adsorption effects on equipment walls may have influenced initial results. In this context, CHAPOY <u>et al.</u> (2005) corrected the water solubility data in the gas phase for the binary methane/water system, initially published in 2003 [3]. This data revision was prompted by inconsistencies pointed out by H. Meijer (Shell Global Solutions), who indicated the underestimation of water content due to adsorption phenomena within the analytical circuit. To address these discrepancies, the authors recalculated vapor-liquid and vapor-hydrate equilibrium values for temperatures between 283.08 K and 318.12 K and pressures up to 35 MPa, adjusted the binary interaction parameters of the NRTL model, and revised equilibrium curves using the Peng-Robinson equation of state with the Trebble-Bishnoi alpha function and classical mixing rules. The new results showed better agreement with the literature, although minor discrepancies still exist at specific temperatures.

Given the importance of accurately measuring moisture content in natural gases and methane- CO_2 mixtures, TORRES et al. (2025) present a comprehensive analysis of experimental methods and thermodynamic models used for this determination. The presence of water in gas systems is a critical factor in predicting hydrate formation, which can block pipelines and compromise operational safety. To mitigate these risks, various measurement techniques are employed, including Gas Chromatography (GC), which, despite being widely used, has limitations in detecting low concentrations of water; Karl Fischer (KF), effective for small moisture quantities but susceptible to chemical interferences; Gravimetric Analyses, which offer precision but are time-consuming and complex; and Chilled Mirror (CM), considered a reference method but prone to contamination by hydrocarbons and alcohols. Advanced techniques such as Quartz Crystal Microbalance (QCM) and Tunable Diode Laser Absorption Spectroscopy (TDLAS) provide rapid and precise measurements, being particularly useful for detecting moisture at low levels. The article also highlights the Differential Scanning Hygrometer (DSH) as a promising innovation, eliminating the need for external calibration and suitable for critical conditions such as CO_2 transport in carbon capture and storage (CCS). In thermodynamic modeling, Cubic Equations of State (CEoS), such as Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK), are widely used in industry but exhibit limitations in accurately representing water due to its strong self-association. More advanced models, such as PC-SAFT (Perturbed-Chain SAFT) and CPA (Cubic Plus Association), demonstrate better performance by accounting for associative interactions of water, making them more effective in predicting moisture content in methane-CO₂ mixtures. Comparisons between experimental data and model predictions indicate that PC-SAFT and CPA offer higher accuracy over a wide range of pressures and temperatures, particularly for CO_2 -rich mixtures where correct estimation of the water dew point is essential. The article concludes that, despite significant advancements in moisture measurement and modeling in natural gases, challenges remain, particularly in obtaining reliable measurements under extreme conditions and continuously improving thermodynamic models to ensure more precise predictions applicable to the oil, gas, and CCS industries.

The difficulty in directly measuring gas moisture in equilibrium with hydrates is also highlighted by BURGASS and CHAPOY (2023), who report that conventional humidity sensors, such as those based on dew point or laser absorption spectroscopy (TDLAS), can exhibit significant errors due to trace water adsorption on internal surfaces of experimental systems. Additionally, ZHANG <u>et al.</u> (2011) emphasize that small temperature and pressure variations can significantly affect hydrate stability, making it challenging to achieve true equilibrium conditions.

Another factor contributing to data scarcity is gas composition dependency. QUEIMADA <u>et al.</u> (2024) demonstrate that impurities such as CO, N₂, and H₂ can significantly alter water solubility and hydrate formation conditions, introducing additional uncertainties in the available data. CHAPOY <u>et al.</u> (2010) reinforce this issue, indicating that CO₂-rich mixtures exhibit different behavior from pure methane, requiring distinct experimental and modeling approaches.

YOUSSEF et al. (2009) present an innovative approach by performing hydratevapor equilibrium measurements without the presence of a liquid phase, using Karl Fischer titration for moisture quantification. However, the obtained results remain limited to specific systems, and extrapolation to multicomponent mixtures remains an open question.

Various thermodynamic approaches have been employed to predict the solubility of water in the gas phase in equilibrium with hydrates. However, these models present limitations, particularly due to the lack of reliable data for calibration and validation. Hydrate-vapor equilibrium modeling is often conducted using cubic equations of state, such as Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR), combined with mixing rules to represent gas-water interactions. The study by CHAPOY et al. (2003) exemplifies the application of the modified Peng-Robinson equation of state (PR-EoS) with the Mathias-Copeman α function and Huron-Vidal mixing rules, incorporating the NRTL local composition model. These approaches allow for an accurate representation of vapor-liquid and vapor-hydrate phase equilibria, which are essential for predicting hydrate formation and optimizing natural gas transportation and production processes. Additionally, water solubility in the gas phase was correlated using Henry's law for the aqueous phase, demonstrating that this approach is only valid above hydrate formation conditions since sorption effects can significantly impact the solubility of hydrocarbons in water at lower temperatures. The study also evaluated SRK with Huron-Vidal (HV) mixing rules, observing
that these approaches exhibited significant deviations for systems containing CO_2 .

As an alternative, the Cubic-Plus-Association equation of state (CPA-EoS) has been widely used due to its ability to represent associative interactions, such as hydrogen bonding. YOUSSEF <u>et al.</u> (2009) demonstrated that the hydrate dissociation temperature strongly depends on the water content in the vapor phase and that the CPA equation of state more accurately predicts equilibrium points by considering the associative interactions of water, whereas SRK requires adjusted binary interaction parameters. The study concludes that thermodynamic modeling based on CPA, combined with the classical Platteeuw and van der Waals model, is suitable for predicting hydrate formation even in the absence of a liquid phase and suggests further investigations for multicomponent systems without an aqueous phase.

CHAPOY <u>et al.</u> (2010) showed that CPA performs better in predicting water solubility in gas in equilibrium with hydrates, especially when combined with solid equilibrium models such as van der Waals and Platteeuw. The authors concluded that the developed thermodynamic model exhibited excellent agreement with experimental data, validating its application for predicting moisture content in methane systems and synthetic mixtures in equilibrium with hydrates. Similar results were obtained by ZHANG <u>et al.</u> (2011), who found that CPA outperformed traditional cubic models, with absolute deviations below 4 ppm in measurements under 40 ppm.

The limited availability of experimental data on hydrate-vapor equilibrium and the challenges in modeling water solubility in gas highlight the need for further studies to improve the calibration and validation of thermodynamic models. Obtaining more precise measurements while minimizing errors associated with moisture adsorption and variations in experimental conditions is essential to reduce uncertainties in available data. Additionally, the development of more robust predictive models, especially for complex mixtures and extreme conditions, is fundamental for industrial applications such as the safe transportation of natural gas and the capture and storage of CO_2 , contributing to more efficient and sustainable processes.

2.3 Multiphase Flash Calculation

Multiphase flash calculation is a technique used in chemical and process engineering to determine phase equilibrium in multicomponent systems. It calculates the distribution of components among different phases (vapor, liquid, and solid) under specific temperature and pressure conditions. This type of analysis is essential in processes such as separation, transportation, and processing of complex mixtures. The calculation is based on thermodynamic equilibrium, where the equality of fugacities between phases defines equilibrium, and mass conservation ensures that the total amount of each component is maintained. The approach employs equations of state (such as Peng-Robinson and PC-SAFT) and phase equilibrium coefficients (K-values) to predict the composition and amount of the present phases.

2.3.1 Thermodynamic Equilibrium

Thermodynamic equilibrium is the state in which a system exhibits constant macroscopic properties over time, indicating the absence of net mass or energy flows between its parts or phases. Additionally, there are no temperature, pressure, or chemical composition gradients within the system [44]. This occurs because, at equilibrium, the driving forces responsible for the transfer of energy, volume, or mass are nullified, resulting in a static equilibrium state where macroscopic properties remain invariant over time. This state can be characterized by three main conditions: thermal equilibrium, in which all phases share the same temperature; mechanical equilibrium, where pressure is equal across phases; and chemical equilibrium, in which the chemical potentials of each component are equal across the different phases. These conditions ensure that the system reaches maximum entropy in closed systems with constant U_{Total} (total internal energy of the system), V_{Total} (total volume of the system), and N_{Total} (total molecule number of the system), or minimum Gibbs free energy in closed systems with equal temperature between phases, equal pressure between phases, and constant N_{Total} [45]. The criterion of maximum entropy is based on postulates that provide the conceptual foundation for the formulation and analysis of thermodynamic systems at equilibrium [46].

In any case, the equilibrium state of a system is fully determined by Nc + 2 variables, and if these variables are intensive, a degree of freedom associated with the system's mass or molecular number is eliminated. In a multiphase system, each phase is considered an open system relative to the others, while the multiphase set as a whole is closed. Maximum entropy is established as the equilibrium criterion, incorporating internal equilibrium with a specified molecular number, internal energy, and volume. Thus, for a system composed of Nc components and Np phases, isolated and without chemical reactions, the conditions of thermal equilibrium (Eq. 2.21), mechanical equilibrium (Eq. 2.22), and chemical equilibrium (Eq. 2.23) must be satisfied, as they are necessary conditions to characterize the equilibrium of the system.

$$T_1 = T_2 = \dots = T_{Np} \tag{2.21}$$

$$P_1 = P_2 = \dots = P_{Np} \tag{2.22}$$

$$\mu_{1,1} = \mu_{1,2} = \cdots = \mu_{1,Np}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad (2.23)$$

$$\mu_{Nc,1} = \mu_{Nc,2} = \cdots = \mu_{Nc,Np}$$

However, these conditions are not necessarily sufficient, as they may represent local minima, maxima, or saddle points. If the global quantity of each component, the system's temperature, and pressure are specified and measurable, the remaining variables become a Gibbs energy minimization problem. For a system in internal equilibrium with Nc components, (Nc - 1) specified mole fractions, and two additional independent intensive variables, its intensive thermodynamic properties can be determined. Thus, a multiphase system will have (Np)(Nc + 2 - 1) independent variables for the entire system, which are related by the necessary conditions of thermal equilibrium ((Np-1) equations), mechanical equilibrium ((Np-1) equations), and chemical equilibrium ((Nc)(Np - 1) equations). Applying Gibbs' phase rule [45] (Eq. 2.24), we arrive at Eq. 2.26, which determines the number of degrees of freedom of the system.

F = (Number of independent variables) - (Number of independent equations)(2.24)

$$F = [Np(2 + Nc - 1)] - [2(Np - 1) + Nc(Np - 1)]$$
(2.25)

$$F = 2 + Nc - Np \tag{2.26}$$

Let F be the number of degrees of freedom of the system. When this number equals 1, the system is called univariant; if it equals 0, it is called invariant. O'CONNELL and HAILE (2005) discusses situations where, although a sufficient number of properties appear to have been chosen to characterize a system, the state is still not uniquely defined, leading to so-called "indifferent states". Such situations can frustrate trial-and-error methods in phase equilibrium problems. The first type occurs when fewer properties than necessary are specified: for example, in a single-component liquid-vapor equilibrium system, determining only temperature and pressure is insufficient to define the vapor fraction, resulting in infinite possibilities along the tie line. A second type arises when the correct number of properties is specified, but they are not independent or become coupled during calculations, as in azeotropes or critical points, where temperature, pressure, and compositions are

interconnected and lose independence.

From the Gibbs-Duhem relation, exposed by TAVARES <u>et al.</u> (2023), variations in temperature, pressure, and the chemical potential of each component can be related, totaling (Nc+2) variables. However, these are interdependent and do not satisfy the (Nc+2) degrees of freedom. Eq. 2.27 presents this relation in generalized form, and Eq. 2.28 applies this relation to Gibbs energy.

$$n\left(\frac{\partial\bar{M}}{\partial P}\right)dP + n\left(\frac{\partial\bar{M}}{\partial T}\right)dT - \sum_{i}^{Nc}N_{i}d\bar{M} = 0$$
(2.27)

Here, n is the total number of moles in the system, \overline{M} is any partial molar property, N_i is the number of moles of component i, and \overline{M}_i is any partial molar property of component i.

$$SdT - VdP + \sum_{i}^{Nc} N_i d\mu_i = 0 \qquad (2.28)$$

When the system's temperature and pressure are specified, Eq. 2.28 reduces to expression 2.29. By deriving any thermodynamic property, Eq. 2.30 is obtained, which states that the summation of the number of moles multiplied by the partial derivative of the chemical potential with respect to any thermodynamic variable at constant temperature and pressure is zero.

$$\sum_{i}^{Nc} N_i d\mu_i = 0 \tag{2.29}$$

$$\sum_{i}^{Nc} N_i \frac{\partial \mu_i}{\partial \zeta} = 0 \tag{2.30}$$

By substituting ζ with the number of moles of a component $k(n_k)$, it is concluded that the number of moles of any component in the same phase j alters the chemical potential of component i. The summation of the product of this variation with the number of moles of component i equals zero, as shown in Eq. 2.31. This form of the Gibbs-Duhem relation is used to eliminate some derivatives when deriving phase equilibrium algorithms based on Gibbs energy minimization.

$$\sum_{i}^{N_c} N_i \frac{\partial \mu_i}{\partial n_k} = 0 \tag{2.31}$$

2.3.2 Multiphase Flash Calculation Method

The multiphase flash calculation method is a fundamental approach for determining phase equilibrium in multicomponent systems under various thermodynamic constraints. This subsection delves into the different types of flash calculations, their underlying principles, and their practical applications in engineering. By analyzing scenarios such as isothermal-isobaric conditions and various specified system parameters, this method enables precise determination of phase compositions and fractions.

In the isothermal-isobaric flash problem (fixed T, P), the phase fractions and compositions in equilibrium are determined at a specified temperature, pressure, and overall composition, with the solution representing the global minimum of Gibbs energy. In the flash $P, \beta_1 \to T, \beta_2$, the overall system composition, pressure, and the relative fraction of phase 1 are specified, and the solution provides the temperature and the relative fraction of phase 2. In the flash $T, \beta_1 \to P, \beta_2$, the overall composition, temperature, and the relative fraction of phase 1 are specified, and the pressure and relative fraction of phase 2 are calculated. Finally, in the flash $\beta 1, \beta 2 \to T, P$, the relative fractions of the phases are specified, and the temperature and pressure are calculated. When the relative fraction of a phase equals zero, that phase is said to be incipient, corresponding to a dew point if the phase is vapor, a bubble point if it is liquid, or a crystallization or precipitation point if it is solid. Figure 2.1 presents the different types of Flash calculations discussed, where the boxes on the left represent the inputs for each model, and the boxes on the right represent the outputs obtained.



Figure 2.1: Illustration of Flash Types.

RACHFORD and RICE (1952) presented an efficient method for calculating

vapor-liquid equilibrium of hydrocarbons during flash vaporization. The described method is based on solving implicit equations, particularly applicable to phase equilibrium in hydrocarbon systems. It relies on the relationship between the mole fractions of components in the liquid and vapor phases using equilibrium coefficients K. The calculation is structured to determine phase ratios and compositions within a closed system, utilizing the mass balance equation. The procedure adopts an iterative and efficient process, divided into segments to locate the root of the equation without relying on derivatives, making it robust against high sensitivity problems. This algorithm was implemented on IBM 604 computers, enabling fast and accurate calculations, including results tabulated to six significant digits in just a few minutes. Finally, the method is presented as a versatile and powerful tool for various types of numerical problems, provided the function involved meets basic criteria of continuity and root uniqueness.

The works of MICHELSEN (1982a) and MICHELSEN (1982b) expand the isothermal flash problem to multiphase systems and include stability analyses. The first paper focuses on verifying thermodynamic stability using the Gibbs tangent plane criterion, identifying whether a mixture can split into multiple phases and providing initial estimates for subsequent calculations. The second paper details numerical methods for phase separation calculations using a single equation of state for thermodynamic modeling. It proposes a stability analysis as an initial step to verify if a phase is stable, followed by iterative methods, such as direct substitution and Newton-Raphson, to optimize phase splitting and minimize Gibbs energy.

2.4 Stability Analysis and Tangent Plane Distance

If a stable mixture can split into multiple phases and these phases are not previously known, methods are needed to minimize the Gibbs free energy to determine whether the mixture will separate into phases and whether those phases are stable. Stability analysis and optimization methods are fundamental for phase equilibrium calculations in scenarios like the one described above. MICHELSEN (1982a) and MICHELSEN (1982b) provide a detailed approach to solving isothermal flash problems, covering both stability analysis and phase splitting calculations. Stability analysis is based on the Gibbs tangent plane criterion, which checks whether the Gibbs free energy of a mixture can be reduced by forming a new phase. To this end, the criterion is evaluated as shown in Eq. 2.32:

$$TPDF = \sum_{i} y_i \left(\mu_i(y) - \mu_i(z) \right) \ge 0$$
 (2.32)

Let TPDF represent the tangent plane distance function, which must be pos-

itive to ensure stability, y, the composition of the test phase, y_i , the composition of component i in the test phase, and z, the overall composition. Instability is identified when the tangent plane at the current composition lies above the Gibbs surface, suggesting the need for phase splitting. To numerically solve the stability criterion, Michelsen presents specific methods, such as direct substitution (linear), which is efficient for systems with low non-ideality. Additionally, accelerated methods like Broyden's method and the General Dominant Eigenvalue Method (GDEM) are recommended, particularly effective near critical points. In multicomponent and multiphase systems, more robust iterative methods are employed, such as Gibbs energy minimization via Newton-Raphson and modified Cholesky decomposition, ensuring convergence even in the presence of indefinite matrices.

The Tangent Plane Distance Function (TPDF) is defined as the vertical distance between the Gibbs free energy surface at a trial composition y and the tangent plane constructed on this surface at a reference composition z. This criterion is fundamental for verifying the stability of a mixture, determining whether phase splitting is necessary. Stability analysis using TPDF requires the global minimization of this function concerning the trial composition y, subject to equality and inequality constraints. If the global minimum value of TPDF(y) is negative, the mixture is unstable. Otherwise, it is stable. This formulation can be transformed into an unconstrained problem by defining new decision variables related to mole fractions. To determine stability, it is necessary to verify that all local minima of the TPDF are non-negative, locating all local minima and confirming that the TPDF value is non-negative at these points. If any negative value is found, the mixture is declared unstable and prone to phase separation.

ZHANG (2011) reviews global optimization methods applied to phase equilibrium modeling and calculations in multicomponent systems, addressing complex problems such as stability analysis, Gibbs free energy minimization, and parameter estimation in thermodynamic models. He highlights that these problems can be formulated as global optimization challenges, requiring robust methods to handle non-convex and highly non-linear functions, especially in multicomponent and multiphase systems. Stability analysis is introduced as an essential step to identify the globally stable thermodynamic state of a mixture. The tangent plane criterion is applied, where the mixture is considered stable if the Gibbs free energy surface is not below the tangent plane. The tangent plane distance function (TPDF) is globally minimized to assess the stability of a mixture. For phase equilibrium calculations, the paper describes two main methods: solving non-linear equations and directly minimizing Gibbs free energy. The first method relies on mass balance equations and equilibrium relations, while the second directly minimizes free energy, offering greater reliability in finding the global equilibrium state. The problem is formulated as shown in Eq. 2.33:

$$G = \sum_{j=1}^{\alpha} \sum_{i=1}^{c} n_{ij} \mu_{ij}$$
(2.33)

subject to mass balance constraints (Eq. 2.34):

$$\sum_{\alpha} n_{ij} = z_i n_F, \quad 0 \le n_{ij} \le z_i n_F \tag{2.34}$$

The article also covers simultaneous chemical and physical equilibrium calculations, formulating additional constraints for chemical element balances and minimizing Gibbs free energy subject to stoichiometric constraints as well as mass balance and chemical reaction constraints. The author emphasizes the use of global minimization because phase equilibrium modeling and calculation problems involve highly non-linear, non-convex functions with multiple local minima, especially in multicomponent and multiphase systems. These challenges make traditional optimization methods, such as those based on local minima, inadequate, as they can lead to trivial or physically unrealistic solutions, compromising the reliability of the results.

GUPTA et al. (1991) presents an innovative approach for simultaneous phase equilibrium and stability calculations in reactive and non-reactive systems. The proposed method integrates the formulation of coupled non-linear equations, enabling the joint analysis of stability and isothermal-isobaric equilibrium in multiphase systems. Using the Newton-Raphson method, the algorithm solves equations related to phase fractions, mole fraction summations, and stability variables, minimizing Gibbs free energy based on chemical potentials. The formulation is based on rigorous criteria to ensure stability, such as Kuhn-Tucker conditions [53], and facilitates the inclusion or exclusion of phases during calculations, which is particularly useful near phase boundaries. The mathematical constraints include material balances for reactive and non-reactive systems, allowing the extension of calculations to different chemical scenarios, from methanol formation to systems containing heavy hydrocarbons. The algorithm is divided into two main loops: an inner loop, which resolves phase fractions and stability, and an outer loop, which calculates mole fractions based on iteratively updated fugacity coefficients. This iterative scheme efficiently addresses multiphase problems, such as the coexistence of liquid and vapor phases in systems near the critical point.

BALLARD and SLOAN (2004) presents a robust algorithm for Gibbs free energy minimization applied to phase equilibrium involving gas hydrates. It covers various phases, including solid, aqueous, liquid hydrocarbon, and vapor phases. The method uses composition-independent distribution coefficients (ideal K-values) to establish initial estimates for the components. These values are applicable to all involved phases, providing a reliable starting point for the iterative process. Convergence is based on the Newton method, ensuring quadratic speed and stability even in systems with pronounced non-ideal behavior. The algorithm also handles specific constraints, such as mass conservation and non-negativity constraints, converting the problem into an unconstrained minimizer using the Lagrange method. The inclusion of additional stability constraints and variables allows the identification and exclusion of fictitious phases ("shadow phases") that do not participate in the actual equilibrium.

SEGTOVICH et al. (2016) proposes a robust algorithm for simultaneous multiphase flash calculations and stability analysis, including hydrate phases. Building on the work of GUPTA et al. (1991) and BALLARD and SLOAN (2004), the algorithm is optimized for speed and robustness, being applicable to systems with different physical states, such as liquid, vapor, ice, and structural hydrates of types sI and sII. Stability analysis is integrated into the flash calculation, allowing simultaneous verification of equilibrium conditions and detection of unstable phases. This approach replaces traditional sequential methods, such as that of MICHELSEN (1982a), ensuring computational efficiency and consistency in results. The algorithm applies the Newton-Raphson method to solve non-linear equations. The iteration involves resolving variables for the present phases (active phases), updating fugacity coefficients and compositions through successive substitution, testing stability variables for convergence, and dynamically adjusting the list of active phases. The algorithm incorporates the concept of "shadow phases", allowing the detection of potential phases that may arise during the iterative process. Phases initially treated as "shadow" can be promoted to real phases if their stability criteria are violated, optimizing the analysis of simultaneous multiple phases.

Comparing the five studies, MICHELSEN (1982a) and MICHELSEN (1982b) establish the foundation for stability analysis through the Gibbs tangent plane criterion, evaluating whether free energy can be minimized by introducing new phases, serving as an initial, robust, and efficient diagnostic method for predicting equilibrium conditions in simple systems. GUPTA et al. (1991) advances this approach by integrating stability calculations directly into the equilibrium algorithm, eliminating the need for separate steps. It employs iterative methods, such as Newton-Raphson, to adjust fugacity coefficients and compositions, incorporating stability criteria based on eigenvalues and stability variables to identify unstable phases during the process. Subsequently, BALLARD and SLOAN (2004) further enhances this approach by consolidating previous techniques into a generalized Gibbs minimization algorithm, which accounts for complex phases, such as sI, sII, and sH hydrates, as well as ice and solid salts. This work also uses stability variables and free energy-

based criteria to monitor incipient phases and automatically adjust compositions and component distributions, ensuring robustness even in highly non-ideal systems. Finally, SEGTOVICH <u>et al.</u> (2016) extends these methodologies to explicitly handle solid phases and structural changes in systems with hydrates and ice, adopting the concept of "shadow phases" to predict incipient phases and manage complex phase transitions.

This work is based on the method presented by SEGTOVICH et al. (2016) to develop the implemented program, discussed in subsequent sections.

2.5 PVTsim Software

PVTsim[®] is a commercial software widely used in the oil and gas industry for fluid property modeling and PVT (Pressure-Volume-Temperature) simulations. It covers a broad range of applications, from reservoir fluid analysis to flow systems and surface process modeling. The Flow Assurance module of PVTsim[®], which was employed in this study, is a specialized tool for analyzing and predicting fluid behavior in flow systems, focusing on ensuring safe and efficient flow. This module is extensively used to identify and mitigate operational issues in oil and gas production systems, such as hydrate formation, wax and asphaltene deposition, and other flowrelated challenges under extreme temperature and pressure conditions.

The software offers nine variations of the cubic equations of state (EoS) Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK), allowing the modification of binary interaction parameters. For high-accuracy gas property predictions, such as Z-factors and dew points, the GERG-2008 EoS is utilized, including flash calculations, phase envelope, and property generation [55].

The software is also capable of simulating hydrate formation conditions in gas and oil mixtures, allowing for the calculation of hydrate formation temperature depression caused by commonly used inhibitors (MeOH, EtOH, MEG, DEG, and TEG) and the assessment of inhibitor loss to hydrocarbon phases [55]. The flash calculation options automatically provide the quantities and types of hydrates (structures I, II, and H), and identify hydrocarbon, aqueous, solid salt, and ice phases.

Chapter 3

Methodology

3.1 Modeling Fluid Phases

Fluid phase modeling was conducted using the cubic Peng-Robinson equation of state, incorporating modifications proposed by AZNAR and SILVA TELLES (1997) and SEGTOVICH (2014), and the PC-SAFT equation of state (Perturbed Chain Statistical Associating Fluid Theory) introduced by GROSS and SADOWSKI (2001).

3.1.1 Generic Cubic Equation of State

Cubic equations of state share a unified mathematical form represented by equation 3.1.

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{(\bar{V} + \varepsilon B)(\bar{V} + \sigma B)}$$
(3.1)

To determine the attraction parameter (A) and co-volume parameter (B), mixing rules and combination rules are applied, following van der Waals fluid theory [57]. The combination rule generates cross-parameters from the pure component parameters. The simplest rules used are the geometric rule for attraction and the arithmetic rule for the co-volume term, employing binary interaction parameters for each pair $(k_{ij} \text{ and } l_{ij})$, as shown in equations 3.2 and 3.3.

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \tag{3.2}$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \tag{3.3}$$

Here, $k_{ii} = 0$ ($\forall i$) and $k_{ij} = k_{ji}$, ensuring consistency with the second Virial coefficient rule. The parameter values were obtained from MEDEIROS et al. (2016)

for the Modified Peng-Robinson equation of state and are presented in Table 3.1. The binary interaction parameters were estimated using experimental vapor pressure data for the pure components, within the temperature range of 58 to 647 K and the pressure range of 1.5×10^{-6} to 22.1 MPa. These cross-parameters allow the global mixture parameters, A and B, to be obtained using mixing rules.

Table 3.1: Binary Interaction Parameters. Adapted from [7], Table 8.

Compound	Water	Carbon Dioxide	Methane	Ethane
Water	0	0.045492	0.514138	—
Carbon Dioxide	0.045492	0	0.095439	0.10349144
Methane	0.514138	0.095439	0	0.0020964
Ethane	_	0.103491	0.002096	0

For this work, the quadratic mixing rule was used to calculate parameters A and B, as shown in equations 3.4 and 3.5.

$$A = \sum_{i}^{C} \sum_{j}^{C} x_i x_j a_{ij} \tag{3.4}$$

$$B = \sum_{i}^{C} \sum_{j}^{C} x_i x_j b_{ij} \tag{3.5}$$

Assuming the commonly used simplification when the mixture molecules do not have highly discrepant dimensions, *i.e.*, when the binary interaction parameter for co-volume is zero $(l_{ij} = 0)$, Eq. 3.5 reduces to Eq. 3.6.

$$B = \sum_{i}^{C} x_i b_i \tag{3.6}$$

For fugacity coefficient calculation, the expression can be derived from the residual Gibbs energy, starting from equation 3.7.

$$\ln \phi_i = \frac{1}{RT} \left[\frac{\partial (n\bar{G}^R)}{\partial N_i} \right]_{T,P,N_{j\neq i}}$$
(3.7)

The expression for \bar{G}^R derives from cubic equations, as shown in equation 3.8.

$$\frac{\bar{G}^R}{RT} = -\ln(Z-\beta) - qI + Z - 1 \tag{3.8}$$

Here, Z is the compressibility factor and can be written as in equation 3.9.

$$Z = \frac{\bar{V}}{\bar{V} - B} - q \frac{B}{(\bar{V} + \epsilon B)(\bar{V} + \sigma B)}$$
(3.9)

Where,

$$q = \frac{A}{BRT} \tag{3.10}$$

$$\beta = \frac{BP}{RT} = Z\rho B \tag{3.11}$$

$$I = \frac{1}{\sigma - \epsilon} \ln \left(\frac{\bar{V} + \sigma B}{\bar{V} + \epsilon B} \right)$$
(3.12)

Obtaining derivatives at constant P is not convenient since Z depends on (\bar{V}) . Using the change of independent variables, as in equation 3.13, and deriving with respect to N_i , while keeping T, V, and $N_{j\neq i}$ constant, leads to expression 3.14.

$$d\frac{n\bar{G}^R}{RT} = \left. \frac{d(n\bar{G}^R/RT)}{dP} \right|_{T,\underline{N}} dP + \left. \frac{d(n\bar{G}^R/RT)}{dT} \right|_{P,\underline{N}} dT + \sum_i \left. \frac{d(n\bar{G}^R/RT)}{dN_i} \right|_{T,P,N_{j\neq i}} dN_i$$
(3.13)

$$\frac{d(n\bar{G}^R/RT)}{dN_i}\Big|_{T,V,N_{j\neq i}} = \left.\frac{d(n\bar{G}^R/RT)}{dP}\right|_{T,\underline{N}} \left.\frac{dP}{dN_i}\right|_{T,V,N_{j\neq i}} + \left.\frac{d(n\bar{G}^R/RT)}{dN_i}\right|_{T,P,N_{j\neq i}} (3.14)$$

Solving the derivatives in Eq. 3.14, applying the combination and mixing rules, along with the simplification applied to expression 3.6, results in Eq. 3.15 for the fugacity coefficient calculation.

$$\ln \phi_i = \frac{\bar{b}_i}{b}(Z - 1) - \ln(Z - \beta) - \bar{q}_i I$$
(3.15)

Where:

$$\bar{q}_i = \left(\frac{\partial(nq)}{\partial N_i}\right)_{T,N_{j\neq i}} = q\left(1 + \frac{\bar{a}_i}{A} - \frac{\bar{b}_i}{B}\right)$$
(3.16)

$$\bar{a}_i = \left(\frac{\partial(nA)}{\partial N_i}\right)_{T,N_{j\neq i}} = 2\sum_j a_{ij}x_j - A \tag{3.17}$$

$$\bar{b}_i = b_i \tag{3.18}$$

$$I = \begin{cases} \frac{1}{\sigma - \epsilon} \ln\left(\frac{\bar{V} + \sigma B}{\bar{V} + \epsilon B}\right), \text{ if } \sigma \neq \epsilon \\ \frac{B}{\bar{V} + \epsilon B}, \text{ if } \sigma = \epsilon \end{cases}$$
(3.19)

Cubic equations of state can be expressed in two forms: explicit in volume or explicit in pressure. The first form directly provides the compressibility factor or volume for a given temperature and pressure, while the second form directly gives the pressure for a given temperature, with the volume calculated indirectly.

When expressed in terms of volume, two sets of roots may emerge: two complex roots and one real root, or three real roots. Only real, positive roots greater than the co-volume parameter b have physical significance. In this context, the largest root corresponds to the vapor phase volume, while the smallest root corresponds to the liquid phase volume. The intermediate root is discarded as it represents a mechanically unstable phase. This instability arises because the derivative of pressure with respect to volume at constant temperature is positive (Eq. 3.20). In other words, a small increase in volume leads to a small increase in pressure, which contradicts observed natural behavior and represents mechanical instability.

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T > 0 \tag{3.20}$$

3.1.2 Peng-Robinson Equation of State

For the Peng-Robinson equation of state, the parameters are defined for pure components based on critical pressure, critical temperature, and acentric factor (ω) [58]. The parameter $\alpha(T)$ is defined as shown in Eq. 3.21.

$$\alpha_i(T) = \left(1 + k_{PR_i} - k_{PR_i} \sqrt{\frac{T}{T_{c_i}}}\right)^2 \tag{3.21}$$

Here, k_{PR_i} is a characteristic expression of the equation of state used, ω is the acentric factor for the pure component, as given by Eq. 3.22, and T_{c_i} is the critical temperature of the pure component.

$$k_{PRi} = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2 \tag{3.22}$$

The parameters σ and ϵ are defined as shown in Eqs. 3.23 and 3.24, respectively, and the parameters b and a are defined as in Eqs. 3.25 and 3.26.

$$\sigma = 1 + \sqrt{2} \tag{3.23}$$

$$\epsilon = 1 - \sqrt{2} \tag{3.24}$$

$$a_i = a_{c_i} \alpha_i(T) \tag{3.25}$$

$$b_i = 0.07780 \frac{RT_{c_i}}{P_{c_i}} \tag{3.26}$$

Here, a_{c_i} represents the critical attraction term, as shown in Eq. 3.27:

$$a_{c_i} = 0.45724 \frac{R^2 T_{c_i}^2}{P_{c_i}} \tag{3.27}$$

Thus, for a mixture, Eqs. 3.4 and 3.5 are transformed into Eqs. 3.28 and 3.29, respectively.

$$A = \sum_{i}^{C} \sum_{j}^{C} x_{i} x_{j} \sqrt{(a_{c_{i}} \alpha_{i})(a_{c_{j}} \alpha_{j})} (1 - k_{ij})$$
(3.28)

$$B = 0.07780R \sum_{i}^{C} x_i \frac{T_{c_i}}{P_{c_i}}$$
(3.29)

3.1.3 Modifications to the Peng-Robinson Equation of State

The implemented modifications were specific to the water component. The modification to the attractive term was based on the proposal by AZNAR and SILVA TELLES (1997), as shown in Eq. 3.30, with the k parameters re-estimated by SEGTOVICH (2014). Additionally, a constant correction factor was introduced for the critical attraction term, $f_{ac_{PR}}^*$, and the co-volume term, $f_{b_{PR}}^*$, as shown in Eqs. 3.31 and 3.32, respectively, and detailed in Table 3.2. The estimation procedure was performed in the temperature range of 0 °C to 100 °C, aiming to adjust the equation of state for low-temperature data while ensuring improved predictive capability within this range and potentially at higher temperatures outside the hydrate formation region.

$$\alpha_w^*(T) = e^{\left[k_1\left(1 - \frac{T}{T_c}\right)\left|1 - \frac{T}{T_c}\right|^{(k_2 - 1)} + k_3\left(\frac{T_c}{T} - 1\right)\right]}$$
(3.30)

$$a_{c_w}^* = f_{ac_{PR}}^* a_{c_w}^{PR}$$
(3.31)

$$b_w^* = f_{b_{PR}}^* b_w^{PR} (3.32)$$

Here, $a_{c_w}^{PR}$ and b_w^{PR} represent the critical attraction and co-volume terms from Eqs. 3.27 and 3.26, respectively.

Table 3.2: Parameters for the Peng-Robinson Equation of State.

$f^*_{ac_{PR}}$	$f_{b_{PR}}^{*}$	k_1	k_2	k_3
9.6039×10^{-1}	8.4850×10^{-1}	8.1638×10^{-1}	1.2822	5.3817×10^{-4}

3.1.4 PC-SAFT Equation of State

The SAFT (Statistical Associating Fluid Theory) equation of state (SAFT EoS) is a theoretical model based on Perturbation Theory developed by Wertheim, which describes fluids using a modular approach. Its current form, known as the "original SAFT", emerged in later publications, and variants such as CK-SAFT, LJ-SAFT, soft-SAFT, and PC-SAFT were proposed to refine the attractive contribution and other features. The model constructs the Helmholtz energy step-by-step: starting with hard spheres, adding attractive potentials (e.g., Lennard-Jones), allowing chain formation, and incorporating specific interactions, such as hydrogen bonding. Each parameter used for a pure compound has physical significance [59].

In this study, the PC-SAFT version proposed by GROSS and SADOWSKI (2001) [8] [60] was used. This version builds upon a theory for chain molecules with squarewell potential, culminating in a model for real chain molecules of any length, from spheres to polymers. Thus, molecules are conceived as chains composed of spherical segments, and the pair potential for a chain segment is defined by a modified squarewell potential, as shown in Eq. 3.33.

$$u(r) = \begin{cases} \infty, \ r < (\sigma - s_1) \\ 3\epsilon, \ (\sigma - s_1) \le r < \sigma \\ -\epsilon, \ \sigma \le r < \lambda\sigma \\ 0, \ r \ge \lambda\sigma \end{cases}$$
(3.33)

Here, u(r) is the pair potential, r is the radial distance between two segments, σ is the temperature-independent segment diameter, ϵ is the potential well depth, and λ is the reduced well width, assuming the ratio $s_1/\sigma = 0.12$.

Non-associative molecules are characterized by three parameters for pure components: the temperature-independent segment diameter (σ), the potential well depth (ϵ), and the number of segments per chain (m). For associative components, two additional parameters are included: the association energy ($\epsilon^{A_iB_i}/k$) and the effective association volume ($\kappa^{A_iB_i}$). This model, although simple, incorporates a step-function for $r < \sigma$ that represents a key characteristic of real molecular behavior: soft repulsion. In other words, molecules acquire a collision diameter σ only at extremely low velocities, where the temperature approaches zero. Otherwise, increasing the temperature results in a smaller collision diameter.

In Perturbation Theory, intermolecular interactions are divided into a repulsive part, calculated using a reference fluid, and an attractive part, treated as a perturbation to the reference system. A rigid chain reference fluid with a temperaturedependent segment diameter (Eq. 3.34) is used to describe the soft repulsion of molecules.

$$d(T) = \int_0^\sigma \left[1 - \exp\left(-\frac{u(r)}{k_B T}\right) \right] dr$$
(3.34)

Here, k_B is the Boltzmann constant, and T is the temperature. Integrating Eq. 3.34, an expression for the temperature-dependent segment diameter for component $i, d_i(T)$, is obtained, as shown in Eq. 3.35.

$$d_i(T) = \sigma_i \left[1 - 0.12 \, \exp\left(-\frac{3\epsilon_i}{k_B T}\right) \right] \tag{3.35}$$

The equation of state, expressed in terms of the Residual Helmholtz Free Energy (Eq. 3.36), comprises four contributions: a hard-chain contribution (A^{hc}) , a dispersion contribution accounting for attractive interactions (A^{disp}) , a hard-sphere contribution (A^{hs}) , and a contribution for molecular association (A^{assoc}) , as shown in Eq. 3.37 [8][60]. The residual Helmholtz free energy (A^{res}) is used as a starting point, as all thermodynamic properties can be derived from it.

$$A^{res} = A^{total} - A^{id} \tag{3.36}$$

The residual Helmholtz energy is the sum of the reference part (A^{ref}) and dispersion part (A^{disp}) , as shown in Eq. 3.37.

$$A^{res} = A^{ref} + A^{disp} \tag{3.37}$$

Here, A^{ref} is given by the contributions of the hard-sphere (A^{hs}) , hard-chain (A^{hc}) , and associative (A^{assoc}) terms, as shown in Eq. 3.38.

$$A^{ref} = A^{hs} + A^{hc} + A^{assoc} \tag{3.38}$$

Thus, the Residual Helmholtz Free Energy can be expressed as Eq. 3.39.

$$A^{res} = A^{hs} + A^{hc} + A^{assoc} + A^{disp}$$

$$(3.39)$$

GROSS and SADOWSKI (2001) use a nomenclature, which will be maintained in this work, where the reduced quantity is denoted with a tilde (\sim) above the property. Therefore, the reduced Residual Helmholtz Free Energy can be defined as in Eq. 3.40. Thus, Eq. 3.39 can be rewritten in terms of the reduced Helmholtz Free Energy in Eq. 3.41.

$$\tilde{a}^{res} = \frac{A^{res}}{Nk_BT} = \frac{\bar{A}^{res}}{RT}$$
(3.40)

$$\tilde{a}^{res} = \tilde{a}^{hs} + \tilde{a}^{hc} + \tilde{a}^{assoc} + \tilde{a}^{disp}$$
(3.41)

Where N is the number of molecules, k_B is the Boltzmann constant, R is the gas constant, and T is the temperature.

Rigid Chain Contribution: The rigid chain contribution is given by Eq. 3.42.

$$\tilde{a}^{hc} = \tilde{m}\tilde{a}^{hs} - \sum_{i} x_i(m_i - 1) \ln g_{ii}^{hs}(\sigma_{ii})$$
(3.42)

Where \tilde{m} is the average number of segments in the mixture, as given in Eq. 3.43.

$$\tilde{m} = \sum_{i} x_i m_i \tag{3.43}$$

The contribution of the Hard-Sphere term is given by Eq. 3.44 for the segments, and the radial distribution function of the Hard-Sphere fluid is provided by Eq. 3.45.

$$\tilde{a}^{hs} = \frac{A^{hs}}{N_s kT} = \frac{1}{\zeta_0} \left[\frac{3\zeta_1 \zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3 (1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right]$$
(3.44)

$$g_{ij}^{hs} = \frac{1}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i + d_j}\right) \frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3}$$
(3.45)

Let ζ_n be defined as in Eq. 3.46.

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n, \quad n \in \{0, 1, 2, 3\}$$
(3.46)

Dispersive Contribution: The dispersive contribution to the Helmholtz Free Energy is given by Eq. 3.47.

$$\tilde{a}^{disp} = -2\pi\rho I_1(\eta,\bar{m})\overline{m^2\epsilon\sigma^3} - \pi\rho\bar{m}C_1I_2(\eta,\bar{m})\overline{m^2\epsilon^2\sigma^3}$$
(3.47)

Here, C_1 is the compressibility expression defined as in Eq. 3.48. The abbreviations used in Eq. 3.47 are provided in Eqs. 3.49 and 3.50.

$$C_1 = \left(1 + z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho}\right)^{-1} = \left(1 + \bar{m} \frac{8\eta - 2\eta^2}{(1-\eta)^4} + \left(1 - \bar{m} \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2}\right)\right)$$
(3.48)

$$\overline{m^2 \epsilon \sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right) \sigma_{ij}^3 \tag{3.49}$$

$$\overline{m^2 \epsilon^2 \sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right)^2 \sigma_{ij}^3 \tag{3.50}$$

Where η is the packing fraction, representing a reduced segment density, defined as

in Eq. 3.46.

Association Contribution: The reduced Helmholtz Free Energy due to association, used for pure components, is a linear average of the mole fractions, as shown in Eq. 3.51 [61] [62].

$$\tilde{a}^{assoc} = \sum_{i} X_i \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right]$$
(3.51)

Where X^{A_i} is the mole fraction of molecules *i* not bound to the site *A*, given by Eq. 3.52.

$$X^{A_i} = [1 + N_{Av} \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j}]^{-1}$$
(3.52)

Where \sum_{B_j} is the sum over all sites of molecule j $(A_j, B_j, C_j, ...)$ and \sum_j is the sum over all components. The density ρ_j is given by Eq. 3.53.

$$\rho_j = X_j \rho \tag{3.53}$$

The association strength $(\Delta^{A_i B_j})$ is given by Eq. 3.54.

$$\Delta^{A_i B_j} = d_{ij}^3 g_{ij} (d_{ij})^{seg} \kappa^{A_i B_j} \left[\exp\left(\frac{\epsilon^{A_i B_j}}{k_B T}\right) - 1 \right]$$
(3.54)

Where $d_{ij} = (d_{ii} + d_{jj})/2$. Similarly to Eq. 3.45, the approximation of the radial distribution function of the segments for rigid-sphere mixtures is provided in Eq. 3.55 and in Eq. 3.56 for similar segments.

$$g_{ij}^{seg}(d_{ij}) \approx g_{ij}^{hs}(d_{ij}) = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj}} \frac{\zeta_2}{(1-\zeta_3)^2} + 2\left[\frac{d_{ii}d_{ii}}{d_{ii}+d_{jj}}\right]^2 \frac{\zeta_2^2}{(1-\zeta_3)^3} \quad (3.55)$$

$$g_{ii}^{seg}(d_{ii}) \approx g_{ii}^{hs}(d_{ii}) = \frac{1}{1-\zeta_3} + \frac{3d_{ii}}{2} \frac{\zeta_2}{(1-\zeta_3)^2} + 2\left[\frac{d_{ii}}{2}\right]^2 \frac{\zeta_2^2}{(1-\zeta_3)^3}$$
(3.56)

Where $d_{ij} = (d_i + d_j)/2$ is the effective collision diameter between rigid spheres of two different components [62]. The terms I_1 and I_2 in Eq. 3.47 are the integrals from perturbation theory, as shown in Eq. 3.57.

For chains with square-well interaction, these integrals are functions of density and the number of segments only. The temperature dependence due to the radial distribution term has been neglected because it exhibits moderate dependence [8]. This allows for the substitution of the integrals by power series in terms of η , where the coefficients are functions of the chain length, as shown in Eqs. 3.59 and 3.60.

$$I_1 = \int_1^\infty \tilde{u}(x) g^{hc}(m, x \frac{\sigma}{d}) x^2 dx = \sum_{i=0}^6 a_i(m) \eta_i$$
(3.57)

$$I_2 = \frac{\partial}{\partial \rho} \left[\rho \int_1^\infty \tilde{u}(x)^2 g^{hc}(m, x \frac{\sigma}{d}) x^2 dx \right] = \sum_{i=0}^6 b_i(m) \eta_i \tag{3.58}$$

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m} - 1}{\bar{m}} a_{1i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} a_{2i}$$
(3.59)

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m} - 1}{\bar{m}} b_{1i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} b_{2i}$$
(3.60)

The coefficients a_{0i} , a_{1i} , a_{2i} , b_{0i} , b_{1i} , and b_{2i} are universal constants adjusted to experimental data of pure components, as shown in Table 3.3. They correct the limitations of the model, such as uncertainties in dispersion properties, errors introduced by the reference equation of state, and the excessive simplification of the molecular model [8].

For the parameters of a pair of different segments, as shown in Eq. 3.61, and segment-segment interactions, as in Eq. 3.62, the conventional Berthelot-Lorentz combination rules were applied, where a binary interaction parameter was introduced to correct the segment-segment interactions of different chains.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{3.61}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \tag{3.62}$$

For the association energy and volume (cross-association), the combination rules suggested by Wolbach and Sandler were applied, as shown in Eqs. 3.63 and 3.64.

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2} \tag{3.63}$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left(\frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{\frac{1}{2} (\sigma_{ii} + \sigma_{jj})} \right)^3$$
(3.64)

The calculation of density (Eq. 3.65) is done iteratively, adjusting the reduced density η until the system pressure matches the calculated pressure. In this regard, an initial value of $\eta = 0.5$ is used for the liquid phase, while for the vapor phase, $\eta = 10^{-10}$. Reduced density values greater than 0.7405 exceed the densest packing values and have no physical significance [8]. Once ρ is calculated, the molar density in $kmol/m^3$ can be determined as shown in Eq. 3.66.

Ta	ble	e 3.3 :	Val	\mathbf{ues}	of	Un	iversal	С	constants.	\mathbf{Est}	imated	by	8	
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i	a_{0i}	a_{1i}	a_{2i}	b_{0i}	b_{1i}	b_{2i}
0	0.9105631445	-0.3084016918	-0.0906148351	0.7240946941	-0.5755498075	0.0976883116
1	0.6361281449	0.1860531159	0.4527842806	2.2382791861	0.6995095521	-0.2557574982
2	2.6861347891	-2.5030047259	0.5962700728	-4.0025849485	3.8925673390	-9.1558561530
3	-26.547362491	21.419793629	-1.7241829131	-21.003576815	-17.215471648	20.642075974
4	97.759208784	-65.255885330	-4.1302112531	26.855641363	192.67226447	-38.804430052
5	-159.59154087	83.318680481	13.776631870	206.55133841	-161.82646165	93.626774077
6	91.297774084	-33.746922930	-8.6728470368	-355.60235612	-165.20769346	-29.666905585

$$\rho = \frac{6}{\pi} \eta (\sum_{i} x_i m_i d_i^3)^{-1}$$
(3.65)

$$\bar{\rho} = \frac{\rho}{N_{Av}} \left(10^{10} \frac{\text{\AA}}{m} \right)^3 \left(10^{-3} \frac{kmol}{mol} \right)$$
(3.66)

The calculation of the fugacity coefficient, as defined in Section 3.1.1, is widely used when expressions for its calculation can be obtained from equations of state, given the known relationships between the PVT properties of the mixture. However, for more advanced equations of state, with development associated with the ensemble A(T, V, N), a more appropriate form for $\ln \phi_i$ is the one expressed by Eq. 3.67, starting from the relation $\bar{G}^{res}(T, P, N) = \bar{A}^{res}(T, V, N) + P\bar{V} - RT - RT \ln Z$.

$$\ln \phi_i = \left(\frac{\partial (n\bar{A}^{res}/RT)}{\partial N_i}\right)_{T,V,N_{j\neq i}} - \ln Z = \left(\frac{\partial (n\tilde{a}^{res})}{\partial N_i}\right)_{T,V,N_{j\neq i}} - \ln Z \qquad (3.67)$$

Where the derivative of the expression in 3.67 can be calculated using the expression in 3.68.

$$\left(\frac{\partial(n\tilde{a}^{res})}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \tilde{a}^{res} + (Z-1) + \left.\frac{\partial\tilde{a}^{res}}{\partial x_i}\right|_{T,V,x_j} - \sum_{j}^{NC} \left[x_j \left.\frac{\partial\tilde{a}^{res}}{\partial x_j}\right|_{T,V,x_i}\right] \quad (3.68)$$

3.2 Modeling of the Ice Phase

The modeling of the ice phase used experimental sublimation pressure measurements as a reference, with the parameters re-estimated by SEGTOVICH (2014) and presented in Table 3.4, and the molar volume of ice, as presented by KLAUDA and SANDLER (2000). The calculation of the fugacity of water in the ice phase is expressed in Eq. 3.69. It is important to note that, in the calculation of the fugacity of water in the ice phase, it is assumed to be pure ice. Therefore, a calculation strategy adopted when there is at least one component in the mixture besides water is to consider the mole fraction of water in the ice phase equal to 1 and the fugacity coefficient of the other components present in the mixture as 1×10^{20} , effectively "expelling" them from the ice phase.

$$f_w^I = P^{Sublim,I} \phi_w^I \exp\left(\frac{\bar{V}_w^I}{RT} (P - P^{Sublim,I})\right)$$
(3.69)

Where $P^{Sublim,I}$ is the sublimation pressure correlation of ice, as shown in Eq. 3.70, f_w^I is the fugacity of water in the ice phase, ϕ_w^I is the fugacity coefficient of the vapor under the sublimation conditions of the ice, and \bar{V}_w^I is the molar volume of water in

the ice phase.

$$P^{Sublim,I} = \exp\left(k_1 \ln T + \frac{k_2}{T} + k_3 + k_4T\right)$$
(3.70)

Table 3.4: Parameters for Ice Sublimation Pressure [9].

k_1	k_2	k_3	k_4
2.0165×10^{0}	-5.9224×10^3	1.7990×10^1	-4.4105×10^{-3}

For the molar volume of ice, Eq. 3.71 was used, and the parameters are presented in Table 3.5.

$$\bar{V}_w^I = l_0 \ln T + l_1 T + l_2 T^2 \tag{3.71}$$

Table 3.5: Parameters for Ice Molar Volume Correlation [10].

l_0	l_1	l_2
1.912×10^{-5}	8.387×10^{-10}	4.016×10^{-12}

Finally, the calculation of the fugacity coefficient of water in the ice phase is expressed in Eq. 3.72.

$$\phi_w^I = \frac{f_w^I}{x_w^I P} \tag{3.72}$$

Where x_w^I is the mole fraction of water in the ice phase.

3.3 Modeling the Hydrate Phase

Natural gas hydrates are crystalline solids formed by water molecules (host) and small molecules present in natural gas (guest). The water molecules interact with each other through hydrogen bonds, forming cavities, and the guest molecules occupy these cavities, stabilizing the structure. The modeling of the hydrate phase is based on statistical thermodynamics, following the work on solid solutions by VAN DER WAALS and PLATTEEUW (1959). A priori, some assumptions are made: the structure is not formed due to the occupants, but an idealized structure is assumed and the occupancy is modeled (Figure 3.1); the clathrated molecules are located inside the cavities, and each cavity can hold only one occupant at a time; the contribution of the molecules to the chemical potential is independent of the occupancy, meaning the occupying molecules do not cause distortions in the cavities.





(a) Empty Structure

(b) Occupied Structure

Figure 3.1: Representation of Gas Hydrate Structures: (a) Empty and (b) Occupied.

The number of cavity i, per number of water molecules, can be defined as shown in Eq. 3.73. In Table 3.6, the proportionality factors for the cavities per structure (sI and sII) are presented.

Structure	ν Small Cavity	ν Large Cavity
sI	2/46	6/46
sII	16/136	8/136

 Table 3.6: Cavity Proportionality Factors.

$$\nu_j = \frac{N_j^{cages}}{N_w} \tag{3.73}$$

Where N_i^{cages} is the number of cavities of type i, N_w is the number of water molecules forming the structure, and ν_i is the number of cavities of type i per water molecule. The clathrated guest molecules in the cavity are restricted to one per cavity, and there is no interaction between neighboring guests. In other words, the movement of a guest molecule inside the cavity is independent of the number of types of guests in the system. Thus, the Hamiltonian of the occupied lattice is expressed in Eq. 3.74.

$$\mathcal{H} = \mathcal{H}_h + \mathcal{H}_g + \mathcal{H}_{hh} + \mathcal{H}_{gg} + \mathcal{H}_{hg} \tag{3.74}$$

Where \mathcal{H} is the total energy of the system (vibrational, rotational, translational degrees of freedom), \mathcal{H}_h is the energy of water (host), \mathcal{H}_g is the energy of the guest

molecule, \mathcal{H}_{hh} is the energy between two water molecules, \mathcal{H}_{gg} is the energy between two guest molecules, and \mathcal{H}_{hg} is the energy between a water molecule and a guest molecule.

Conveniently starting from the canonical partition function (canonical ensemble) to incorporate the previous assumptions, we have that the partition function is the product of three factors: the water lattice structure (Q^{EL}) , the distribution of guests in the cavities (W_j) , and the states of the guest molecules $(Q(T, V, \underline{N}))$, assumed to be an ideal gas. Thus, the partition function for the water lattice (Empty Lattice) is expressed in Eq. 3.75 and 3.76, the function describing the state of two guest molecules in equation 3.77, and for N molecules of type *i* in cavity *j*, in equation 3.78.

$$A^{EL} = -k_B T \ln(Q^{EL}) \tag{3.75}$$

$$Q^{EL} = \exp\left(\frac{-A^{EL}}{k_B T}\right) \tag{3.76}$$

In the case of Eq. 3.77, the factorial product in the denominator takes into account the indistinguishability of the molecules. However, in the case of clathrates, the type of cavity distinguishes the guest molecules, eliminating the need for the factorial product in the denominator, as shown in Eq. 3.78.

$$Q(T, V, N_1, N_2) = \frac{q_1^{N_1} q_2^{N_2}}{N_1! N_2!}$$
(3.77)

$$Q(T, V, \underline{N}) = \prod_{j} q_{j}^{N_{j,i}}$$
(3.78)

The distribution of guests in the cavities is the permutation of the number of ways that $N_{1,i}$ can be placed into L distinct boxes, as shown in Eq. 3.79.

$$W_1 = \frac{L!}{(L - N_{1,i})! N_{1,i}} \tag{3.79}$$

Where $L = \nu_i N_w$ represents the distinct boxes of type *i* with only one occupant (Figure 3.1 (b)), and $N_{j,i}$ are indistinguishable objects. Eq. 3.79 transforms into Eq. 3.80.

$$W_j = \frac{\nu_i N_w!}{(\nu_i N_w - N_{1,i})! \Pi_j N_{j,i}!}$$
(3.80)

Multiplying Eqs. 3.76, 3.78, and 3.80, the model for the canonical partition function obtained by VAN DER WAALS and PLATTEEUW (1959) is reached, as expressed in Eq. 3.81.

$$Q(T, V, \underline{N}) = \exp\left(\frac{-A^{EL}}{k_B T}\right) \prod_{i} \frac{\nu_i N_w!}{(\nu_i N_w - \sum_j N_{j,i})! \prod_j N_{j,i}!} \prod_j q_j^{N_{j,i}}$$
(3.81)

However, since $Q(T, V, \underline{N})$ is a natural function of \underline{N} , it does not remain constant as more guests occupy the cavities *i*. Therefore, we must use the grand canonical partition function with respect to the guest molecules (and semi-grand canonical with respect to the water molecules), which can be obtained as a standard transformation from statistical mechanics starting from Eq. 3.82.

$$\Xi(T, V, \underline{\mu}_j, N_w) = \sum_{N_{j,i}} Q \exp\left(\frac{\mu N_{j,i}}{k_B T}\right)$$
(3.82)

Where $\mu_j = k_B T ln(\lambda_j)$ and k_B is the Boltzmann constant. Thus, Eq. 3.82 transforms into Eq. 3.83.

$$\Xi(T, V, \underline{\mu}_j, N_w) = \sum_{N_{j,i}} Q\lambda^{N_{j,i}}$$
(3.83)

Where λ_j is the absolute activity of component j on an exponential scale. The summation over $N_{j,i}$ accounts for all the distributions of each variable $N_{j,i}$, where $N_{j,i} \geq 0 \ (\forall i, j)$, and the number of empty cavities of type i can be related to the cavities of type j occupied by molecule i by Eq. 3.84.

$$\sum_{j} N_{j,i} + N_{EL,j} = \nu_j N_w \tag{3.84}$$

Substituting Eq. 3.81 into Eq. 3.83, we arrive at Eq. 3.85.

$$\Xi(T, V, \underline{\mu}_j, N_w) = \exp\left(\frac{-A^{EL}}{k_B T}\right) \sum_{N_{j,i}} \prod_i \frac{\nu_i N_w!}{(\nu_i N_w - \sum_j N_{j,i})! \prod_j N_{j,i}!} \prod_j q_j^{N_{j,i}} \lambda^{N_{j,i}} \quad (3.85)$$

Considering the summation of Eq. 3.85 for only one cavity (Small: i=s) and only two types of guests, A and B, plus the empty lattice ($\lambda^{EL} = 1$), we arrive at Eq. 3.86.

$$\Xi(T, V, \underline{\mu}_{j}, N_{w}) = \exp\left(\frac{-A^{EL}}{k_{B}T}\right) \sum_{j=A}^{B} \frac{\nu_{s} N_{w}!}{(\nu_{s} N_{w} - \sum_{j} N_{j,s})! \prod_{j=A}^{B} N_{j,i}!} \prod_{j=A}^{B} q_{j}^{N_{j,s}} \lambda^{N_{j,s}}$$
(3.86)

Expanding the product for two types of guests and one cavity, the expression 3.87 becomes 3.87.

$$\Xi(T, V, \underline{\mu}_{j}, N_{w}) = Q^{EL} \sum_{j=A}^{B} \frac{\nu_{s} N_{w}!}{(\nu_{s} N_{w} - N_{A,s} - N_{B,s})! N_{A,s}! N_{B,s}!}$$

$$q_{A}^{N_{A,s}} \lambda^{N_{A,s}} q_{B}^{N_{B,s}} \lambda^{N_{B,s}} 1^{(\mu_{s} N_{w} - N_{A} - N_{b})}$$
(3.87)

The Multinomial Theorem, a generalization of the Binomial Theorem, applicable for the expansion of powers of a sum involving more than two terms, $(x_1 + x_2 + ... + x_m)^N$, describes how to express it as a sum of products of the individual powers of the terms x_m , as in Eq. 3.88.

$$(x_1 + x_2 + \dots + x_m)^N = \sum_{N=n_T} \frac{N!}{n_1! \dots n_m!} x_1^{n_1} \dots x_m^{n_m}$$
(3.88)

Comparing Eq. 3.87 and Eq. 3.88, the right-hand side of the first equation, the summation term, is equivalent to the right-hand side of the second equation. Therefore, Eq. 3.87 simplifies to Eq. 3.89.

$$\Xi(T, V, \underline{\mu}_j, N_w) = Q^{EL} (1 + q_A \lambda_A + q_B \lambda_B)^{\nu_s N_w}$$
(3.89)

Generalizing for all cavities i and all guests j, equation 3.89 becomes as shown in Eq. 3.90.

$$\Xi(T, V, \underline{\mu}_j, N_w) = Q^{EL} \prod_i^{n_{cage}} (1 + \sum_j^{n_{guest}} q_{j,i} \lambda_{j,i})^{\nu_i N_w}$$
(3.90)

Applying the natural logarithm on both sides of the equation, we finally arrive at the expression for the semi-grand canonical partition function with respect to the water molecules in Eq. 3.91.

$$\ln \Xi(T, V, \underline{\mu}_{j}, N_{w}) = \ln Q^{EL} + \sum_{i}^{n_{cage}} \nu_{i} N_{w} \ln(1 + \sum_{j}^{n_{guest}} q_{j,i} \lambda_{j,i})$$
(3.91)

3.3.1 Calculation of the Chemical Potential of Water in Hydrates

The goal is to derive an expression to calculate the chemical potential of water, enabling phase equilibrium calculations. Equation 3.91 represents a grand canonical partition function with respect to the occupants (μ_j fixed) and a grand canonical function with respect to water molecules (N_w specified). By defining a state function $\Psi(T, V, N_w, \mu_j)$ as the Legendre transform of the Helmholtz free energy, we obtain Eq. 3.92.

$$\Psi(T, V, N_w, \mu_j) = A - \sum_j N_j \left(\frac{\partial A}{\partial N_j}\right)_{T, V, N_w}$$
(3.92)

By solving Eq. 3.92, we arrive at expression 3.93. Applying the differential to both sides of the Eq. 3.93 yields Eq. 3.94.

$$\Psi(T, V, N_w, \mu_j) = A - \sum_j \mu_j N_j$$
(3.93)

$$d\Psi(T, V, N_w, \mu_j) = -SdT - PdV + \mu_w^H dN_w - \sum_j N_j d\mu_j$$
(3.94)

Thus, the relationship of Eq. 3.91 with classical thermodynamics can be expressed as Eq. 3.95.

$$d(k_B T \ln \Xi) = S dT + P dV + \sum_j N_j d\mu_j - \mu_w^H dN_w$$
(3.95)

Thus, the chemical potential of water in the occupied structure can be given by deriving expression 3.95 with respect to the number of water molecules (Eq. 3.96) and the number of molecules of type j in Eq. 3.97.

$$\mu_w^H = -k_B T \left(\frac{\partial \ln \Xi}{\partial N_w}\right)_{T,V,\mu_j} \tag{3.96}$$

$$N_{j} = k_{B}T \left(\frac{\partial \ln \Xi}{\partial \mu_{j}}\right)_{T,V,N_{w},\mu_{i\neq j}} = \lambda_{j} \left(\frac{\partial \ln \Xi}{\partial \lambda_{j}}\right)_{T,V,N_{w},\mu_{i\neq j}}$$
(3.97)

Solving Eq. 3.97 from Eq. 3.91, we obtain an expression that calculates the number of guest molecules of type j. Since N_j is equivalent to $\sum_j N_{ji}$, the number of molecules j in cavities of type i, we have the expression 3.98.

$$N_{ji} = \frac{\nu_i N_w q_{ji} \lambda_j}{1 + \sum_j q_{ji} \lambda_j} \tag{3.98}$$

We define a variable Θ_{ji} as the probability of finding a molecule of type j in a cavity of type i, *i.e.*, the occupancy factor of a given molecule in cavity i, as shown in Eq. 3.99.

$$\Theta_{ji} = \frac{N_{ji}}{\nu_i N_w} = \frac{q_{ji}\lambda_j}{1 + \sum_j q_{ji}\lambda_j}$$
(3.99)

Eq. 3.96 can be solved by substituting equation 3.91 into the expression and performing the necessary algebraic manipulations, resulting in Eq. 3.100.

$$\mu_w^H - \mu_w^{EL} = -k_B T \sum_i \nu_i \ln(1 + \sum_j q_{ji} \lambda_j)$$
(3.100)

Eq. 3.99 can be simplified by finding expressions for the absolute activity λ_j and the individual partition function of the individual particle q_{ji} in terms of adjusted or experimentally measured parameters. In this sense, for an ideal gas, the canonical partition function Q^{PIG} can be given by Eq. 3.101 and the chemical potential by Eq. 3.102.

$$Q^{PIG} = \frac{1}{N!} q^N \tag{3.101}$$

$$\mu^{o} = -k_{B}T \left(\frac{\partial \ln Q^{PIG}}{\partial N}\right)_{T,V} = -k_{B}T \ln \frac{q}{N}$$
(3.102)

Assuming the separability for the individual particle partition function q into a translational part and another part containing the internal energy modes (Eq. 3.103), where equation 3.104 expresses the translational part.

$$q = q_{trans}q_{int} \tag{3.103}$$

$$\frac{q_{trans}}{N} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{V}{N} \tag{3.104}$$

Where h is Planck's constant and m is the particle mass. The square root of the term in parentheses is called the thermal de Broglie wavelength. Since for an ideal gas $V/N = k_B T/P$, substituting equation 3.103 and equation 3.104 into equation 3.102, we arrive at expression 3.105.

$$\mu^{o} = -k_{B}T \ln\left[\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{3/2} k_{B}T\right] - k_{B}T \ln q_{int} + k_{B}T \ln P \qquad (3.105)$$

On the other hand, the chemical potential is defined relative to a standard chemical potential, as expressed by Eq. 3.106.

$$\mu = \mu^o + k_B T \ln\left(\frac{f_i}{P}\right) \tag{3.106}$$

Where μ^{o} is the standard chemical potential. Substituting Eq. 3.105 into Eq. 3.106 and performing the necessary algebraic steps, Eq. 3.107 is reached for the chemical potential, with the absolute chemical potential expressed by Eq. 3.108.

$$\mu = -k_B T \ln\left(\frac{f_i}{k_B T (2\pi m k_B T/h^2)^{3/2} q_{int}}\right)$$
(3.107)

$$\lambda = \frac{f_i}{k_B T (2\pi m k_B T / h^2)^{3/2} q_{int}}$$
(3.108)

Defining a constant C_{ji} , the Langmuir constant, as in Eq. 3.109, and substituting Eq. 3.108 into the expression, the individual partition function and the absolute activity can be taken into account. The denominator of Eq. 3.109 contains the internal part of the partition function and the ideal gas contribution, while the division also considers the non-ideality effect.

$$C_{ji} = \frac{q_{ji}\lambda j}{f_j} = \frac{q_{ji}}{k_B T (2\pi m k_B T / h^2)^{3/2} q_{int}}$$
(3.109)

Thus, equation 3.99 can be rewritten in terms of the Langmuir constant as expressed in Eq. 3.110.

$$\Theta_{ji} = \frac{C_{ji}f_j}{1 + \sum_j C_{ji}f_j} \tag{3.110}$$

By definition, the sum of all probabilities is equal to 1, as shown in equation 3.111.

$$\sum_{j} \Theta_{ji} = \sum_{j} \frac{C_{ji} f_j}{1 + \sum_{j} C_{ji} f_j} = 1$$
(3.111)

Eq. 3.111 can be rewritten as Eq.3.112.

$$1 - \sum_{j} \Theta_{ji} = 1 - \sum_{j} \frac{C_{ji} f_j}{1 + \sum_{j} C_{ji} f_j}$$
(3.112)

Applying the natural logarithm on both sides of expression 3.112 and performing the necessary algebraic manipulations, we arrive at Eq. 3.113.

$$\ln(1 - \sum_{j} \Theta_{ji}) = -\ln(1 + \sum_{j} C_{ji} f_j)$$
(3.113)

Substituting equations 3.109 and 3.113 into Eq. 3.100, we obtain an expression for the calculation of the difference between the chemical potential of water in the occupied structure and the chemical potential of water in the empty structure in molecular units as a function of the occupation factor, as shown in equation 3.114.

$$\mu_w^H - \mu_w^{EL} = \Delta \mu^{H-EL} = k_B T \sum_i \nu_i \ln(1 - \sum_j \Theta_{ji})$$
(3.114)

Rescaling the expression 3.114 to molar units, we finally obtain the expression

3.115.

$$\Delta \mu^{H-EL} = RT \sum_{i} \nu_i \ln(1 - \sum_{j} \Theta_{ji})$$
(3.115)

The molar composition of the components in the hydrate phase can be calculated from a simple mass balance and normalized relative to the number of water molecules using Eq. 3.116 and Eq. 3.117.

$$x_j^H = \frac{\sum_i \nu_i \Theta_{ji}}{1 + \sum_i \sum_j \nu_i \Theta_{ji}}$$
(3.116)

$$x_w^H = \frac{1}{1 + \sum_i \sum_j \nu_i \Theta_{ji}} \tag{3.117}$$

3.3.2 Calculation of the Langmuir Constant

Following the hypothesis of VAN DER WAALS and PLATTEEUW (1959), where the encapsulated particle can rotate freely in the cavity, meaning that the interaction between the guest molecule and the molecules of the cavity wall is weak, it can be assumed that its rotational partition function is the same as that of an ideal gas, as shown in Eq. 3.118.

$$q_{ji} = \Phi_j(T)q_{int} \int_{cell} \exp\left[\frac{-\bar{w}(r)}{k_B T}\right] dV$$
(3.118)

Where q_{ji} is the rotational partition function, $\Phi_j(T)$ is the same term previously defined for an ideal gas for the translational contribution and internal degrees of freedom of the encapsulated particle, q_{int} is the internal partition function, and the third term, the integral, represents the free volume for the displacement of the guest molecule within the cavity. Assuming the cavity potential has spherical symmetry (Figure 3.2) as proposed by Lennard-Jones-Devonshire [63], and converting the integral in expression 3.118 into spherical coordinates, we arrive at Eq. 3.119.

$$q_{ji} = \Phi_j(T)q_{int} \int_0^{2\pi} \int_0^{\pi} \int_0^R \exp\left[\frac{-\bar{w}(r)}{k_B T}\right] r^2 \sin\theta dr d\theta d\phi \qquad (3.119)$$

Where R is the radius of the free cavity and r is the distance from the guest molecule to the center of the cavity. Solving the integral and substituting expression 3.119 into Eq. 3.109, we arrive at an expression for the Langmuir constant (Eq. 3.120) in terms of the potential of the molecules within the cavities.

$$C_{ji} = \frac{4\pi}{k_B T} \int_0^R \exp\left[\frac{-\bar{w}(r)}{k_B T}\right] r^2 dr \qquad (3.120)$$



Figure 3.2: Illustrative Representation of the Sphericity of the Cavity.

Where $\bar{w}(r)$ is the average interaction potential in the cavity. For the potential, the Kihara potential was used, as shown in equations 3.121 and 3.122.

$$\bar{w}(r) = 2z\epsilon \left[\frac{\sigma^{12}}{R^{11}r} \left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5r} \left(\delta^4 + \frac{a}{R}\delta^5\right)\right]$$
(3.121)

$$\delta^{N} = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right]$$
(3.122)

Where z is the coordination number, σ is the distance from the core to zero potential, a is the radius of the spherical core, ϵ is the maximum attractive potential, and $N \in (4, 5, 10, 11)$. These parameters are called Kihara parameters (occupation parameters), and their values are presented in Table 3.7.

 Table 3.7: Occupancy Parameters.

Molecule	a (Å)	σ (Å)	ϵ/k_B (°K)	Reference
CH_4	0.300	3.2398	153.17	[11]
C_2H_6	0.5651	3.2541	176.91	[64]
CO_2	0.6805	2.9718	168.27	[64]

The physical properties of the lattice, according to the type of structure formed,

are those used by PARRISH and PRAUSNITZ (1972) and are presented in Table 3.8.

	Structure sI	Structure sII
Ideal Composition	$M_1 3 M_2 32 \mathrm{H}_2 \mathrm{O}$	$M_1 2 M_2 17 \mathrm{H}_2 \mathrm{O}$
Number of water		
molecules	46	136
Number of small		
cavities	2	16
Number of large		
cavities	6	8
Small cell diameter		
(Å)	7.95	7.82
Large cell diameter		
(Å)	8.60	9.46
Small coordination number		
(z)	20	20
Large coordination number		
(z)	24	28

 Table 3.8: Physical Properties of the Hydrate Lattice [11].

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3.3.3 Relative Chemical Potential between the Empty Lattice and Pure Water

The modeling for calculating the relative chemical potential between the empty lattice and pure water (liquid or ice) is based on the expressions presented by HOLDER et al. (1980). Starting from the thermodynamic relation for a pure substance (Eq. 3.123), and integrating, it is possible to express the relative chemical potential between the empty lattice and pure water, in the liquid or ice condition, as shown in equation 3.124.

$$d\left(\frac{\mu}{RT}\right) = -\frac{\bar{H}}{RT^2}dT + \frac{\bar{V}}{RT}dP \qquad (3.123)$$

$$\Delta \mu_w^{EL-PW} = RT \left[\frac{\Delta \mu_0^{EL-PW}(T_0, P_0)}{RT_0} - \int_{T_0}^T \left(\frac{\Delta \bar{H}^{EL-PW}}{RT^2} \right) dT + \int_{P_0}^P \left(\frac{\Delta \bar{V}^{EL-PW}}{RT} \right) dP \right]$$
(3.124)

Where $\Delta \mu_0^{EL-PW}$ is a parameter, $\Delta \bar{H}^{EL-PW}$ is the difference in enthalpy between the empty lattice and pure water in the ice or liquid condition and calculated by expression 3.125, $\Delta \bar{V}^{EL-PW} = \bar{V}^{EL} - \bar{V}^{PW}$ is the difference between the molar volume of the empty lattice and pure water in the ice or liquid condition.

$$\Delta \bar{H}^{EL-PW} = \Delta \bar{H_0}^{EL-PW} + (\Delta C p_0 - \Delta B_0 T_0)(T - T_0) + \Delta B_0 \left(\frac{T^2}{2} - \frac{T_0^2}{2}\right) \quad (3.125)$$

The reference condition, T_0 and P_0 , used for the hydrate phase was the experimental triple point of water, 273.179 K and 612.619 Pa, respectively [12]. The molar volume of the empty lattice is expressed by Eq. 3.126 [66], the molar volume of pure water in the ice condition is given by the correlation presented in section 3.2, and the molar volume of water in the liquid condition is expressed in Eq. 3.127 [66].

$$\frac{\bar{V}^{EL}}{(m^3 mol^{-1})} = [11.8 + 5.39 \cdot 10^{-5} (T/K) + 1.78 \cdot 10^{-6} (T/K)^2]^3 \cdot \left(\frac{10^{-30} N_A}{46}\right) \cdot \exp[-1.098 \cdot 10^{-10} \cdot (P/Pa - 101325)]$$

$$(3.126)$$

$$\frac{\bar{V}^{LW}}{(m^3 mol^{-1})} = [1.00453 \cdot 10^{-10} (T/K)^2 - 5.71157 \cdot 10^{-8} (T/K) + 2.61517 \cdot 10^{-5}] \cdot \exp[3.30859 \cdot 10^{-10} \cdot (P/Pa - 101325)]$$

$$(3.127)$$

Where the reference temperature and pressure used are 273.15 K and 101325 Pa [67]. The values used for $\Delta \bar{H_0}^{EL-PW}$, $\Delta \mu_0^{EL-PW}$, and $\Delta C p_0^{EL-PW}$ are presented in Table 3.9. For the parameter ΔB_0^{EL-PW} , the non-optimized value of 0.1339 $J \cdot mol^{-1}K^{-1}$ was used.

Table 3.9: Parameters of Thermodynamic Properties of the Unoccupied Structure in Relation to Pure Water, in Ice or Liquid Condition [12].

Thermodynamic Formation Property	Structure		
	\mathbf{sI}	\mathbf{sII}	
$\Delta \mu_0^{\text{EL-PW}} (\text{J} \cdot \text{mol}^{-1})$	1264	883	
$\Delta h_0^{\mathrm{EL-PW}(\mathrm{L})} \ (\mathrm{J} \cdot \mathrm{mol}^{-1})$	-4858	-5201	
$\Delta h_0^{\mathrm{EL-PW(I)}} (\mathrm{J} \cdot \mathrm{mol}^{-1})$	1151	808	
$\Delta c p_0^{\mathrm{EL-PW}(\mathrm{L})} \ (\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1})$	-39.16	-39.16	
$\Delta c p_0^{\mathrm{EL-PW}(\mathrm{I})} \ (\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1})$	0.00	0.00	

3.3.4 Fugacity Coefficient of the Hydrate Phase

Given the thermodynamic conditions and the fugacities of the guest molecules calculated, the Langmuir constants can be determined. From there, the occupancy factor of the structure and the relative chemical potential between the water in the occupied structure and the water in the empty lattice can be calculated. With the equations of state and the model for ice, the fugacity of water in the reference condition (pure ice or liquid) is calculated, and thus, the relative chemical potential between the water in the unoccupied structure and the water in the pure liquid or ice condition can be determined. Based on the definition of fugacity Eq. 3.128 [45], for the water component, and integrating between two conditions, H (water in the occupied structure) and PW (pure water, liquid or ice), for the same temperature, we arrive at the expression 3.129.

$$d\left(\frac{\mu_i}{RT}\right) = d(\ln f_i) \tag{3.128}$$

$$f_w^H = f_w^{PW} \exp\left(\frac{\Delta \mu_w^{H-EL} + \Delta \mu_w^{EL-PW}}{RT}\right)$$
(3.129)

Where f_w^H is the fugacity of water in the occupied structure, f_w^{PW} is the fugacity of water in the pure liquid or ice condition, $\Delta \mu_w^{H-EL} = \mu_w^H - \mu_w^{EL}$, and $\Delta \mu_w^{EL-PW} = \mu_w^{EL} - \mu_w^{PW}$. Thus, from the fugacity of pure water and the relative potentials, it is possible to calculate the fugacity of water in the occupied structure. The fugacity coefficient of the components can then be calculated using Eq. 3.130.

$$\phi_i^H = \frac{f_i^H}{Px_i^H} \tag{3.130}$$

Where ϕ_i^H is the fugacity coefficient of component *i* in the occupied structure, f_i^H is the fugacity of component *i* in the occupied structure, and x_i^H is the phase composition of component *i* in the occupied structure.

For the calculation of f_i^H , a numerical trick was used that involves calculating the fugacity of component *i* in the first interaction using the composition of the vapor phase and/or hydrate-forming liquid phase as an initial guess, along with the fugacity coefficient of the vapor phase and/or hydrate-forming liquid phase, followed by the rigorous calculation of the composition in the hydrate phase (x_i^H) , and finally calculating ϕ_i^H using Eq. 3.130. This approach is possible because, at each pressure and temperature condition, part of the composition of component *i* in the vapor phase (or hydrate-forming liquid phase) is consumed and attracted to the cavity of the structure, in thermodynamic equilibrium.

3.4 Multiphase Flash with Stability Analysis

The equations of the multiphase flash algorithm with stability analysis derive from the minimization of the total Gibbs free energy of the system. It essentially involves obtaining the relative phase fractions and the compositions of each phase present in equilibrium, specified by the global composition and two additional intensive variables such as T and P, which represent the global minimum for the Gibbs free energy. The equality of temperature (thermal equilibrium), the equality of pressure (mechanical equilibrium), and the equality of fugacities between phases are necessary but not sufficient conditions for the minimum of the Gibbs free energy. Knowing in advance which phases are possible under the given conditions, within a possible universe, a stability analysis methodology becomes necessary. The present work is based on the methodology of BALLARD and SLOAN (2004), GUPTA et al.(1991), and SEGTOVICH et al.(2016), which seeks a solution to a constrained minimization problem, with all phase fractions being non-negative, resulting in a set of nonlinear equations to be satisfied. The details of the methodology will be presented below.

3.4.1 Minimization of Total Gibbs Free Energy

In a system with T, P, and N specified, the spontaneity condition is given by the decrease in the Gibbs free energy of the system, reaching equilibrium when this energy is minimal with respect to all possible variations. Therefore, it is necessary to find the minimum of the Gibbs free energy, given the constraint that no relative phase fraction can be negative.

Assuming that the macroscopic thermodynamic properties are uniformly distributed within each phase, *i.e.*, there are no gradients along the entire phase and no variations over time, and assuming that there is no chemical reaction — the amount of each component in the system is constant — the total Gibbs free energy of the multiphase system can be expressed by Eq. 3.131.

$$G = \sum_{i} \sum_{j} n_{ij} \mu_{ij} \tag{3.131}$$

Where G is the total Gibbs free energy of the system, n_{ij} is the amount of component i in phase j, and μ_{ij} is the chemical potential of component i in phase j. Eq. 3.131 can be rewritten by specifying a reference phase (Eq. 3.132), and the number of moles of component i in the reference phase is given by Eq. 3.133.

$$G = \sum_{i} n_{i,ref} \mu_{i,ref} + \sum_{i} \sum_{j \neq ref} n_{ij} \mu_{ij}$$
(3.132)
$$n_{i,ref} = Nc_i - \sum_i \sum_j n_{ij} \tag{3.133}$$

Where Nc_i is the number of moles of component *i* in the system, $n_{i,ref}$ is the number of moles of component *i* in the reference phase, and $\mu_{i,ref}$ is the chemical potential of component *i* in the reference phase. A negative relative phase fraction has no physical meaning, thus imposing a physical constraint on the problem, as shown in equation 3.134.

$$\beta_j \ge 0 \tag{3.134}$$

Where β_j is the relative fraction of phase j. This variable can be calculated by Eq. 3.135, and the total number of moles of phase j is given by Eq. 3.136.

$$\beta_j = \frac{Np_j}{Ns} \tag{3.135}$$

$$Np_j = \sum_i n_{ij} \tag{3.136}$$

Where Np_j is the total number of moles of phase j, and Ns is the total number of moles in the system, given by Eq. 3.137.

$$Ns = \sum_{i} Nc_i \tag{3.137}$$

Rewriting Eq. 3.132 by eliminating the variable $n_{i,ref}$, the constrained minimization problem becomes:

min
$$G = \sum_{i} Nc_{i}\mu_{i,\text{ref}} + \sum_{i} \sum_{j \neq \text{ref}} n_{ij}(\mu_{ij} - \mu_{i,\text{ref}})$$

subject to: $\beta_{j} \ge 0$ (3.138)

A slack variable, ς_j , is introduced to transform the inequality constraints into equality. This variable represents the amount of slack for the constraint to be satisfied, *i.e.*, if $\varsigma_j > 0$, it means that the constraint is not fully satisfied (there is a margin of unused constraint). On the other hand, when $\varsigma_j = 0$, the constraint is satisfied, *i.e.*, it is active, as shown in equation 3.139. Here, the slack variable is squared to ensure that it is non-negative, maintaining a physical meaning.

$$\varsigma_j^2 - \beta_j = 0 \tag{3.139}$$

The constrained minimization problem can be transformed into an unconstrained minimization problem by applying the Lagrange method, a powerful mathematical technique for solving optimization problems with constraints. In this method, auxiliary variables called Lagrange multipliers (denoted by λ_i for each constraint of the problem) are introduced and incorporated into the function to be minimized (in this case, the Gibbs free energy), forming a new function called the Lagrangian, \mathcal{L} . This method allows identifying local minima of the Gibbs free energy over the boundary of the domain, where an incipient phase ($\beta_j = 0$) occurs, meaning that the solution for the global minimum of G is not a stationary point but represents a stationary point of \mathcal{L} . Therefore, considering the reference phase as present, the Lagrangian function for the optimization problem is given by Eq. 3.140.

$$\mathcal{L} = G + \sum_{j \neq ref} \lambda_j (\varsigma_j^2 - \beta_j) \tag{3.140}$$

3.4.2 Optimality Condition

When the problem involves inequality constraints, such as $\beta_j \leq 0$, we use the Karush-Kuhn-Tucker (KKT) conditions [53]. These generalize the Lagrange conditions by incorporating inequalities. Applying the 1st Order KKT condition, namely that the derivative of \mathcal{L} with respect to each independent variable (ς_j , λ_j , n_{ij}) equals zero (stationarity), the derivative of the Lagrangian with respect to λ_j (Eq. 3.141) leads to Eq. 3.142.

$$\frac{\partial \mathcal{L}}{\partial \lambda_j} = 0 \tag{3.141}$$

$$\varsigma_j = \sqrt{\beta_j}, \ \forall \ j \neq ref \tag{3.142}$$

Differentiating the Lagrangian with respect to the slack variable (Eq. 3.143), we obtain Eq. 3.144.

$$\frac{\partial \mathcal{L}}{\partial \varsigma_j} = 0 \tag{3.143}$$

$$\varsigma_j \lambda_j = 0, \ \forall \ j \neq ref \tag{3.144}$$

Eq. 3.144 is called the complementary slackness condition in optimization literature [52], where if the Lagrange multiplier is zero, the slack variable is greater than zero. On the other hand, if the Lagrange multiplier is greater than zero, the slack variable is equal to zero and consequently, the constraint is active. Differentiating \mathcal{L} with respect to the variables n_{ij} (Eq. 3.145), we arrive at expression 3.146.

$$\frac{\partial \mathcal{L}}{\partial n_{ij}} = 0 \tag{3.145}$$

$$\frac{\partial G}{\partial n_{ij}} = \lambda_j \frac{\partial \beta_j}{\partial n_{ij}} \tag{3.146}$$

Solving the derivative on the left-hand side of Eq. 3.146 from Eq. 3.138, and knowing that in phase j, the amount of component i affects the chemical potential of the others, we arrive at Eq. 3.147.

$$\frac{\partial G}{\partial n_{ij}} = (\mu_{ij} - \mu_{i,ref}) + \sum_{k} n_{kj} \frac{\partial \mu_{kj}}{\partial n_{ij}}$$
(3.147)

Since the second term on the right-hand side of the equation is exactly the Gibbs-Duhem relation, expression 3.147 reduces to the difference between the chemical potential of component i in phase j and the chemical potential of component i in the reference phase, as shown in Eq. 3.148.

$$\frac{\partial G}{\partial n_{ij}} = (\mu_{ij} - \mu_{i,ref}) \tag{3.148}$$

Solving the partial derivative of the right-hand term in Eq. 3.146 from expression 3.135, we arrive at Eq. 3.149.

$$\frac{\partial \beta_j}{\partial n_{ij}} = \frac{1}{Ns} \tag{3.149}$$

Substituting equations 3.148 and 3.149 into Eq. 3.146, we get Eq. 3.150.

$$(\mu_{ij} - \mu_{i,ref})Ns = \lambda_j \tag{3.150}$$

Defining a variable, θ_j , called the stability variable as in Eq. 3.151, and substituting into equation 3.150, we arrive at Eq. 3.152.

$$\theta_j = \frac{\lambda_j}{NsRT} \tag{3.151}$$

$$\theta_j = \frac{\mu_{ij} - \mu_{i,ref}}{RT} \tag{3.152}$$

Rewriting Eq. 3.152 in terms of fugacity, we get Eq. 3.153.

$$\theta_j = \ln\left(\frac{f_{ij}}{f_{i,ref}}\right) \tag{3.153}$$

Rewriting the equation that expresses the complementary slackness condition (Eq. 3.144), we get Eq. 3.154.

$$\sqrt{\beta_j} N s R T \theta_j = 0 \tag{3.154}$$

By performing the necessary algebraic manipulations, Eq. 3.154 transforms into

Eq. 3.155.

$$\beta_j \theta_j = 0 \tag{3.155}$$

When the stability variable equals zero, the equality of fugacities and chemical potentials is verified, meaning that phase j is in equilibrium with the other phases in the system, and β_j will be greater than zero (present phase) or equal to zero (incipient phase). When θ_j is greater than zero, phase j will not be present - the fugacity of the non-present phase will be greater than that of the reference phase (necessarily present) - and β_j will necessarily be zero, called the shadow phase. This is a theoretical phase that does not stabilize the system, as each component in this phase presents a chemical potential different from the chemical potential of the same components in the reference phase. The molar fractions of the components in this phase are optimal values for \mathcal{L} and for the difference in Gibbs free energy required for the incipient formation of this phase. Therefore, if this composition represents a local minimum in \mathcal{L} and θ_j is greater than zero, no composition close to this will stabilize the system.

3.4.3 Generalized Rachford-Rice Equations

A variable, K-values, called the distribution coefficient, is defined in equation 3.156. By using the definition of fugacity coefficient and the stability variable, and performing the necessary algebraic manipulations, we arrive at Eq. 3.157.

$$K_{ij} = \frac{\phi_{i,ref}}{\phi_{ij}} \tag{3.156}$$

$$x_{ij} = x_{i,ref} K_{ij} e^{\theta_j} \tag{3.157}$$

Summing the terms of Eq. 3.157 over all components, we obtain Eq. 3.158.

$$\sum_{i} x_{ij} = \sum_{i} x_{i,ref} K_{ij} e^{\theta_j}$$
(3.158)

Since these are molar fractions, the sum must equal 1, as shown in equation 3.159, including for the reference phase in Eq. 3.160.

$$\sum_{i} x_{ij} = 1 \tag{3.159}$$

$$\sum_{i} x_{i,ref} = 1 \tag{3.160}$$

Substituting Eq. 3.159 into Eq. 3.158 and subtracting from Eq. 3.160, and

performing the necessary manipulations, we arrive at Eq. 3.161.

$$\sum_{i} [x_{i,ref}(K_{ij}e^{\theta_j} - 1)] = 0$$
(3.161)

Writing the mass balance by component for the phases (Eq. 3.162) and specifying the reference phase, we obtain Eq. 3.163.

$$\sum_{j} \beta_j x_{ij} = z_i \tag{3.162}$$

$$\beta_{ref}x_{i,ref} + \sum_{j \neq ref} \beta_j x_{ij} = z_i \tag{3.163}$$

Where z_i is the global composition of component *i* in the system. Dividing and multiplying the left-hand side of equation 3.163 by $x_{i,ref}$, we get Eq. 3.164.

$$\left(\beta_{ref} + \sum_{j \neq ref} \beta_j \frac{x_{ij}}{x_{i,ref}}\right) x_{i,ref} = z_i \tag{3.164}$$

Substituting equation 3.157 into equation 3.164 and isolating $x_{i,ref}$, we arrive at Eq. 3.165.

$$x_{i,ref} = \frac{z_i}{\beta_{ref} + \sum_{l \neq ref} \beta_l K_{il} e^{\theta_j}}$$
(3.165)

Using the relation $\beta_{ref} = 1 - \sum_{j \neq ref} \beta_j$, we obtain Eq. 3.166.

$$x_{i,ref} = \frac{z_i}{1 + \sum_{l \neq ref} \beta_l (K_{il} e^{\theta_j} - 1)}$$
(3.166)

Substituting equation 3.166 into equation 3.157, we arrive at Eq. 3.167.

$$x_{ij} = \frac{z_i K_{ij} e^{\theta_j}}{1 + \sum_{l \neq ref} \beta_l (K_{il} e^{\theta_j} - 1)}$$
(3.167)

Substituting Eq. 3.166 into Eq. 3.161, we obtain a set of nonlinear algebraic equations 3.168, Res_j , to be satisfied for each phase j except the reference phase.

$$Res_{j} = \sum_{i} \frac{z_{i}(K_{ij}e^{\theta_{j}} - 1)}{1 + \sum_{l \neq ref} \beta_{l}(K_{il}e^{\theta_{j}} - 1)}$$
(3.168)

3.5 Computational Implementation and Resolution Algorithm

The program was developed in Python 3.10, using the Google Colaboratory development environment and VSCode. The thermodynamic models were imple-

mented computationally applying the object-oriented programming paradigm [12] [69]. A base class was defined for calculating the fugacity coefficients of each component in a given phase (Figure 3.3), encapsulating certain common attributes, such as temperature and pressure, which served as a parent class for the specialized subclasses. These specialized or child classes inherit attributes from the parent class, adding specific behavior (calculate_phi()) to calculate the fugacity coefficient (ϕ). The calculate_phi() method, present in all classes, is polymorphic, varying the behavior according to the specific class.



Figure 3.3: UML Diagram for Calculating the Fugacity Coefficients of Each Component in a Given Phase.

The class HydratePhaseComponent() functions as an independent class that relates to the parent class (PhaseComponent) in the use of the chosen equation of state for calculating the fugacity coefficient of pure liquid water. This implemented structure facilitates the code's expansion, allowing the addition of new types of phases or equation of state models without modifying the existing code. The Modified Peng-Robinson equation of state also utilized these concepts in its implementation (Figure 3.4), creating the class PengRobinsonMod(), which encapsulates the methods and attributes related to the Modified Peng-Robinson Equation of State.



Figure 3.4: UML Diagram for the Modified Peng-Robinson Equation of State.

The class protects the internal functions (helper methods) that do not need to be called directly by the user. Methods like $_f_Aalpha()$ and $_f_b()$, for example, are private methods (indicated by _) used internally only. The class can be easily reused or extended for other equations of state, simply by overriding methods such as pressure() and volume() in subclasses. For the PC-SAFT equation of state, an open-source software package (FeOs) was used, developed to implement equations of state (EoS) and Helmholtz energy functionals in classical density functional theory (DFT) by REHNER <u>et al.</u> (2023). The standard PC-SAFT model implemented in FeOs is based on the seminal work of GROSS and SADOWSKI (2001) with improvements for associative and polar systems [60] [71] [72]. FeOs was primarily developed in the Rust programming language, chosen for its efficiency, safety, and support for functional programming, with a complete Python interface built using the PyO3 library, which allows compiling the Rust code as a Python module.

The resolution algorithm is shown in Figure 3.5, with some adaptations from the approach proposed by SEGTOVICH et al. (2016). In the present work, the flash calculation used is of the type $P, \beta_1 \rightarrow T, \beta_2$, initializing the calculations with z_i , P, and β_1 specified, assuming certain phases as present ($\theta_j = 0$), and initial guesses for temperature and phase compositions. An auxiliary loop was used with a defined pressure range, and for each new calculation, the stability variable is computed to check if a given phase continues to be present at the next point. If not, a new phase

is assumed to be present, and the previously calculated values $(x_{ij}^k, T^k, \beta_j^k)$ are used to initialize the next iteration.



Figure 3.5: Flowchart of the Solution Algorithm.

The algorithm contains two loops: an inner loop in the calculation of the Res_j function, which uses the Newton-Raphson method for its solution, and a more external loop to update the phase composition, which uses the method of successive substitution for its solution. Figure 3.6 shows the flowchart of the computational implementation, designed to predict liquid, gas, and solid phases, including hydrates

and ice. It includes a list of thermodynamic properties (critical temperature, T_c , and enthalpy, ΔH) and specific parameters (k_{ij}) , essential for modeling molecular interactions and equilibrium calculations. The code contains two main equations of state models: the Modified Peng-Robinson, suitable for hydrocarbon systems and common mixtures, and PC-SAFT, focused on complex systems, such as those involving polar, associative compounds or mixtures containing water. The code separates phases into three groups: liquid and vapor phases, modeled with the equations of state, and solid phases (hydrate and pure ice), with specific models for each solid.



Figure 3.6: Diagram of the Computational Implementation.

The final output is the calculation of the multiphase equilibrium, combining the results from the liquid, gas, and solid phases. This calculation provides the distribution of components in each phase, allowing for accurate predictions under various operational conditions.

Chapter 4

Results and Discussion

In this chapter, the results obtained and their respective discussions are presented. First, a survey of data available in the literature for the water content in hydrate-vapor equilibria is conducted. Following this, calculations of the water content in gas in equilibrium with hydrate are presented. Subsequently, simulations for different equilibrium scenarios - methane + water, ethane + water, and CO_2 + water - are provided and compared with the results obtained using the PVTsim[®] software, which employed the Peng-Robinson model in the simulations.

4.1 Analysis of Collected Data

Initially, a bibliographic review effort was conducted to gather hydrate-vapor equilibrium data that also reported the water content present in the gas. This information is of utmost importance [38] [42] [73], as in gas-dominated systems, it becomes a key factor for the formation of these crystalline solids and provides a solid foundation for deciding whether to implement a gas line dehydration unit. Furthermore, identifying gaps in these data can guide future experimental studies.

The Table 4.1 presents experimental data on water content in gas in equilibrium with hydrates within the gas-hydrate coexistence region, characteristic of gasdominated systems. The data are organized by types of pure gases (methane, ethane, and carbon dioxide) and include pressure and temperature ranges, as well as water concentration (y_w) expressed in parts per million. The data was also grouped using a clustering algorithm. The algorithm employs K-Means to identify patterns and potential gaps in experimental data, considering variables such as temperature, pressure, and water content. First, the data is loaded and preprocessed, removing missing values. Then, a preliminary study using the Elbow and Silhouette methods helps determine the optimal number of clusters, enabling efficient data segmentation [74]. After selecting k, the algorithm applies K-Means, assigning each point to a cluster and identifying regions with higher dispersion or data absence. For better visualization, the clusters are represented in a temperature versus pressure plot, using distinct colors and covariance ellipses, which highlight the distribution of points around each cluster centroid (Figure 4.1, Figure 4.2, and Figure 4.3). The use of these ellipses allows the identification of regions with low experimental representation, revealing potential gaps in the literature. The algorithm can be dynamically adjusted for different datasets, facilitating exploratory analysis and aiding decisionmaking for new experimental data collection.

Mix	P (MPa)	T (K)	y_w (ppm)	Reference
CH_4	10.010 - 35.090	283.08 - 293.11	0.092 - 225	[2]
	3.44	250.95 - 275.75	32.3 - 243.4	[1]
	6.89	250.55 - 279.15	14.8 - 170.6	[1]
	3.45 - 13.79	238.15 - 272.95	7.1 - 197.8	[38]
	3.45 - 5	260.0 - 278.4	182 - 227	[39]
C_2H_6	2.483	276.15 - 283.65	364 - 564	[5]
	1.51 - 3.75	278.08 - 293.11	215 - 595	[4]
	1.5 - 2.48	271.3 - 280	292 - 455	[39]
$\rm CO_2$	0.69 - 3.45	251.75 - 278.65	89 - 488.5	[6]
	0.91 - 2.23	255.35 - 275.05	198 - 425	[75]
	2.0 - 2.1	260.7 - 276.3	119.4 - 357	[39]

Table 4.1: Water Content in Equilibrium With Hydrate.

For methane, Table 4.1 shows a wide pressure range (3.44 MPa to 35.09 MPa), which covers a significant operational range, and a wide variation in temperature (238.15 K to 293.11 K). The water content suggests that at higher pressures and lower temperatures, the solubility of water in methane is significantly lower, as expected for nonpolar gases.

Analizing Figure 4.1, five clusters were identified with a very clear separation, along with some widely spaced points, especially at high pressures (higher than 25 MPa), at high temperatures (higher than 280 K). Cluster 4 occupies conditions of low pressure and intermediate temperatures, while cluster 1 covers a wide temperature range (240 K to 260 K) at low pressures ($\simeq 8$ MPa). There is a gap at lower temperatures (lower than 240 K), which is an area of interest in gas-dominated systems, and there is also limited information at intermediate pressures (15 MPa to 25 MPa) in the temperature range of 260 K to 280 K. The high-pressure region has a significant information gap in the temperature range of 240 K to 280 K. Additionally, clusters 2 and 5 cover a narrow temperature range, with only a few experimental points.



Figure 4.1: Distribution of Data Clusters for Methane, Illustrating the Relationship Between Average Temperature and Pressure. The ellipses highlight areas of higher data density while also revealing regions with limited experimental coverage.

Ethane shows a larger gap in pressure and temperature, with pressures ranging from 1.5 MPa to 3.75 MPa and temperatures in the range of 271.3 K to 293.11 K, as observed in Table 4.1. This indicates that the experimental data reported for ethane are within a smaller operational range, remaining close to room temperature (293.15 K). It is also observed that ethane exhibits higher water solubility in the gas phase. Analyzing Figure 4.2, four clusters were identified. Clusters 1 and 5 dominate the low-pressure region (below 2 MPa), with a gap at lower temperatures (below 275 K). Between 2 MPa and 3 MPa, there is good data coverage in the temperature range of 275 K to 290 K. Above 3 MPa, there is good data coverage at higher temperatures (above 285 K) but with a gap in the temperature range of 240 K to 285 K. Regarding the temperature distribution, there is good coverage at intermediate temperatures (276 K to 291 K), while temperatures below 275 K, especially at intermediate pressures ($\simeq 2$ MPa to 3 MPa), are poorly represented.



Figure 4.2: Data Clusters for Ethane, Representing the Relationship Between Average Temperature and Pressure. The ellipses indicate the distribution of the clusters, highlighting regions with higher data concentration and gaps in experimental coverage.

For carbon dioxide, the pressure range varies from 0.69 MPa to 3.45 MPa, and the temperature range varies from 251.75 K to 278.65 K. As observed in Figure 4.3, four clusters were identified. Clusters 2 and 3 are found at low pressure, while clusters 1 and 4 are located at high pressure. In the high-pressure range (greater than 3 MPa), fewer data points are available, which may be due to CO_2 condensing at high pressures. However, in the intermediate pressure range ($\simeq 2$ MPa to 3 MPa), which is a region of interest in gas-dominated systems, there are also significant gaps. The highest data density is at pressures below 2.5 MPa, with significant gaps between clusters 1 and 2, and between clusters 2 and 3. Data coverage is better in the temperature range of 257 K to 276 K, with few data points for temperatures below 255 K, especially in the pressure range of 1.5 MPa to 3 MPa.



Figure 4.3: Data Clusters for Carbon Dioxide, Showing the Relationship Between Average Temperature and Pressure. The ellipses represent the distribution of the clusters, highlighting regions with higher data concentration and revealing gaps in experimental coverage, especially at intermediate pressures.

Experimental data are essential for calibrating and validating hydrate formation prediction algorithms for more complex mixtures and multiphase systems. However, the data available in the literature present significant gaps regarding hydrate-vapor equilibrium, which can limit the direct application of these results to more complex scenarios, particularly under subcooling conditions, making it challenging to predict behavior in broader situations.

Subcooling conditions are particularly relevant in the operation of gas-dominated systems, which are common in natural gas exploration in deep waters, such as in the Pre-Salt exploration wells. Gas exits the well at high pressure and temperature and, upon reaching the seabed region, undergoes an abrupt variation in pressure and temperature, entering the hydrate region of the phase envelope [25].

The data collected from the literature review were used in the simulations of this study, presented later, to validate hydrate formation predictions for gas-dominated systems and to assess the algorithm's ability to calculate water content under given thermodynamic conditions.

4.2 Estimation of PC-SAFT Parameters for Pure Components

The estimation of parameters for the pure components of the PC-SAFT equation of state was performed to achieve better predictions of water content, presenting optimized parameters for the equation of state. The data used for the estimation are presented in Tables 4.2 and 4.3. Table 4.2 contains correlation data from the best available data [12].

Temperature (K)	Pressure (Pa)	Volume (dm^3mol^{-1})
273.15	610.5	0.01800
278.15	872.2	0.01800
283.15	1228.0	0.01801
293.15	2338.0	0.01803
303.15	4243.0	0.01808
313.15	7376.0	0.01814
323.15	12330.0	0.01822
333.15	19920.0	0.01831
343.15	31160.0	0.01841
353.15	47340.0	0.01852
363.15	70100.0	0.01865
373.15	101300.0	0.01878

Table 4.2: Saturation Pressure and Molar Volume Data for Water. [12].

Component	Nexp	Temperature (K)		Pressure (MPa)	
		T_{min}	T_{max}	P_{min}	P_{max}
Methane (CH_4)	52	90.69	190.56	0.013	4.6
Ethane (C_2H_6)	50	92	190	1.7×10^{-6}	0.135
Carbon Dioxide (CO_2)	29	216.58	303	0.518	7.183

Table 4.3: Experimental Data of Pure Components Vapor Pressure [13].

The estimation procedure carried out in this work used the least squares objective function, as shown in Eq. 4.1.

$$F_{obj} = \sum_{i}^{Nexp} (\nu_i^{exp} - \nu_i^{calc})$$

$$(4.1)$$

Let ν_i^{exp} represent the measured property value, and ν_i^{calc} represent the property value calculated by the model for a given experiment *i*.

4.2.1 Estimation for Water

The association scheme considered for water in the present work was the 4C model, with two electron donor sites and two electron acceptor sites [76]. A total of five parameters were used and estimated: the temperature-independent segment diameter (σ), the potential depth (ϵ), the number of segments per chain (m), the association energy ($\epsilon^{A_i B_i}/k$), and the effective association volume ($\kappa^{A_i B_i}$).

For saturation pressure, the comparative analysis between the results obtained before (Figure 4.4) and after (Figure 4.6) the parameter estimation for water shows significant improvements in the prediction of vapor saturation pressure (P_{sat}), especially at the experimental triple point of water (273.15 K and 610.5 Pa) [12]. Before optimization, Figure 4.4 and Figure 4.5), which includes an expanded view to facilitate the visualization of the mentioned discrepancy, more evident discrepancies were observed in the low-temperature and low-pressure region, particularly concerning the sublimation pressure (P_{sub}), which did not intersect the saturation pressure curve at the triple point.



Figure 4.4: Saturation Pressure and Sublimation Pressure Before Parameter Estimation. The blue line represents the values calculated by PC-SAFT for the saturation pressure, while the orange line corresponds to the sublimation pressure calculated by the empirical equation for ice. The blue points indicate the experimental data for the saturation pressure (Table 4.2).



Figure 4.5: Zoom-in Figure of the Graph for Saturation Pressure and Sublimation Pressure Before Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure, while the orange line corresponds to the sublimation pressure calculated by the empirical equation for ice. The blue points indicate experimental data for the saturation pressure (Table 4.2).

Figures 4.6 and 4.7 present the data for saturation pressure and sublimation pressure calculated after the parameter estimation was performed. A better alignment between the experimental and calculated data is observed, particularly in the range where the largest discrepancy was noted before the estimation (270 K to 290 K), as shown in Figure 4.7. This demonstrates that the adjusted parameters successfully captured the molecular interactions of water. The average absolute relative deviation (AARD) was 0.87 %, with an absolute relative deviation (ARD) ranging from 0.039 % to 1.78 %.



Figure 4.6: Saturation Pressure and Sublimation Pressure After Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure, while the orange line corresponds to the sublimation pressure calculated by the empirical equation for ice. The blue points indicate experimental data for the saturation pressure (Table 4.2).



Figure 4.7: Zoom-in Figure of the Graph for Saturation Pressure and Sublimation Pressure After Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure, while the orange line corresponds to the sublimation pressure calculated by the empirical equation for ice. The blue points indicate experimental data for the saturation pressure (Table 4.2).

Figures 4.8 and 4.9 correspond to the calculation of the liquid molar volume before and after parameter estimation, respectively. Comparing the two figures, improvements are also observed after the estimation, particularly in the range of 280 K to 350 K. The AARD for these data was 0.25 %, with absolute relative deviations ranging from 0.031 to 0.48. It can be concluded that the behavior predicted by the model, after parameter optimization, more faithfully follows the trend observed experimentally.



Figure 4.8: Liquid Molar Volume Before Parameter Estimation. The green line represents the values calculated by the PC-SAFT for the liquid molar volume and The blue points indicate experimental data for the saturation pressure (Table 4.2).



Figure 4.9: Liquid Molar Volume After Parameter Estimation. The green line represents the values calculated by the PC-SAFT for the liquid molar volume and The blue points indicate experimental data for the saturation pressure (Table 4.2).

4.2.2 Estimation for Hydrocarbons and Carbon Dioxide.

For methane, ethane, and carbon dioxide, a simpler model is considered, where these species are treated as non-associative components, *i.e.*, as inert gases. In this model, the parameters include only the temperature-independent segment diameter (σ) , the potential depth (ϵ) , and the number of segments per chain (m).

Figures 4.10, 4.11 and 4.12 present the data for saturation pressure calculated after the parameter estimation was performed for these compounds. Methane exhibited ARD's ranging from 0.78 to 4.22, while ethane showed deviations in the range of 0.84 to 10.85. Carbon dioxide presented the smallest deviation, ranging from 0.032 to 1.54. The parameters after estimation are shown in Table 4.4.



Figure 4.10: Saturation Pressure of Methane After Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure and the blue points indicate experimental data for the saturation pressure (Table 4.3).



Figure 4.11: Saturation Pressure of Ethane After Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure and the red cross indicate experimental data for the saturation pressure (Table 4.3).



Figure 4.12: Saturation Pressure of Carbon Dioxide After Parameter Estimation. The blue line represents the values calculated by the PC-SAFT for the saturation pressure and the blue points indicate experimental data for the saturation pressure (Table 4.3).

Pure Component	m	σ	ϵ	$\epsilon^{A_i B_i}/k$	$\kappa^{A_iB_i}$
Methane	1.00129951	3.6977732	150.0300173	-	_
Ethane	1.60476474	3.53724799	191.42	-	-
Carbon Dioxide	2.63745077	2.54254214	150.02405597	-	-
Water	1.1281558	2.90022706	210.99179644	1920.02	0.0425

Table 4.4: Estimated Pure Component Parameters for PC-SAFT

4.3 Water Content for the CH₄ and Water System in Gas-Dominated Conditions

Figure 4.13 shows the performance of the PC-SAFT and Modified Peng-Robinson (Modified PR) state models in predicting the water content in hydratevapor equilibrium (HVE) for the CH_4+H_2O system at two distinct pressures: 68.9 bar and 34.4 bar. The simulated results were compared with experimental data available in the literature [1]. These results use modified PR parameters presented in Chapter 3 including k_{ij} , and PC-SAFT parameters estimated as presented in Section 4.2 with k_{ij} equal to zero. At both pressures, the PC-SAFT model demonstrated superior performance compared to the Modified PR model, showing significantly smaller deviations from the experimental data. At the higher pressure (68.9 bar), the PC-SAFT model was particularly effective, with an AARD of only 3.43 %, while the Modified Peng-Robinson model achieved an AARD of 10.52 %. At the lower pressure, the PC-SAFT model also exhibited greater accuracy than the Modified Peng-Robinson model, with an AARD of 8.55 % compared to 18.51 % for the Peng-Robinson model. The Modified Peng-Robinson model exhibited larger deviations at both pressures, highlighting a limitation in capturing the $CH_4 - H_2O$ interactions under the analyzed conditions. This may be related to the model's difficulty in adequately describing intermolecular forces, such as hydrogen bonding, which are fundamental for correctly representing the behavior of systems containing water. Both models showed a decrease in performance as the pressure decreased, which can be attributed to non-ideality effects of the vapor and specific interactions between water and methane molecules.



Figure 4.13: Water content in Methane at Pressure 68.9 bar e 34.4 bar in Hydrate-Vapor Equilibrium; (- -) Mod PR, (...) PC-SAFT; Experimental Data: 68.9 bar (\blacktriangle) and 34.4 bar (\blacklozenge) [1].

Figure 4.14 presents the results for predicting the water content in hydratevapor equilibrium (HVE) at different temperatures (283.08 K, 288.11 K, and 293.11 K). At the lowest temperature (283.08 K), the Modified Peng-Robinson model performed better, with a significantly lower AARD (4.83 %) compared to that of PC-SAFT (12.80 %). At intermediate temperatures, both models exhibited low performance with relatively high deviations (23.54 % for PC-SAFT and 34.94 % for Modified Peng-Robinson). However, PC-SAFT performed better than the Modified PR model, indicating greater sensitivity to temperature changes in the intermediate region. At the highest temperature (293 K), the PC-SAFT model performed better, with an AARD of 7.49 % compared to 10.27 % for the Modified Peng-Robinson model, suggesting greater efficiency under conditions where intermolecular forces are less pronounced due to increased thermal energy.



Figure 4.14: Water content in Methane at Temperature 283.08 K, 288.11 K e 293.11 K in Hydrate-Vapor Equilibrium; (- -) Mod PR, (...) PC-SAFT; Experimental Data: 283.08 K (\blacktriangle), 288.11 K (\blacklozenge), and 293.11 K (\bigstar) [2].

It can also be observed that, for methane in equilibrium with hydrates, the reduction in temperature leads to a lower capacity of the gas to dissolve water, which favors hydrate formation [1]. This is in accordance with previous studies, such as CHAPOY et al. (2003), CHAPOY et al. (2010), and ZHANG et al. (2011), indicating that, for gases like methane, pressure has a lesser effect on water solubility in the gas, with temperature being the predominant factor. Overall, for the CH_4+H_2O system, the PC-SAFT model demonstrated greater accuracy at higher pressures and elevated temperatures, because of its ability to model specific interactions, such as hydrogen bonding, and its higher sensitivity to temperature, especially under intermediate conditions, resulting in higher deviations. On the other hand, the Modified PR model showed more satisfactory performance at lower temperatures and moderate pressures, struggling to capture the system's behavior under more extreme conditions. The presented results are predictive, with no direct correlation to experimental data. Furthermore, the parameters, especially those of PC-SAFT, were estimated under conditions different from those applied in this analysis.

4.3.1 Phase Diagram for the CH_4 and Water System

Figure 4.15 presents the phase diagram for the $CH_4 + H_2O$ system, highlighting the hydrate dissociation conditions as a function of temperature and pressure for different water contents (32.3 ppm, 47.7 ppm, and 126.1 ppm). A decrease in water content shifts the dissociation curve to more extreme conditions, meaning that lower water contents require a lower temperature at a given pressure to stabilize the hydrate structure [12] [43], an effect also observed in experimental data [3][1]. The black lines describe the three-phase equilibrium $H_2O(L)+CH_4(V)+H$, for a system with excess water. The colored curves represent the two-phase hydrate-vapor equilibrium, where the amount of water is below the saturation condition, fully dissolved in the vapor phase, and no longer forms an aqueous phase. The water content in the gas is "consumed" to form the hydrate structure as the condition for the formation of this crystalline solid is reached.



Figure 4.15: Dissociation Conditions for Methane Hydrate; (-.-) Mod PR, (- -) PC-SAFT, (...) PVTsim^(R); Experimental Data: (\times) [3]; (\blacksquare), (\triangleleft), and (\blacklozenge) [1].

The results modeled by the Modified Peng-Robinson (Mod PR), PC-SAFT, and PVTsim[®] methods were compared with experimental data extracted from the literature [3] [1]. All three models showed good agreement with the experimental data at moderate pressures, demonstrating good accuracy in predicting hydrate formation conditions. However, PVTsim[®] exhibited greater deviations at higher pressures (above 15 MPa).

4.4 Water Content for the C_2H_6 and Water System in Gas-Dominated Conditions

Figure 4.16 presents the water content in hydrate-vapor equilibrium (HVE) for the C₂H₆+H₂O system at different temperatures (278.08 K, 283.11 K, 293.11 K, and 298.11 K). The PC-SAFT and Modified Peng-Robinson (Mod PR) models were evaluated and compared with experimental data [4]. The results use the modified PR parameters presented in Chapter 3, including k_{ij} , and PC-SAFT parameters estimated as presented in Section 4.2 with k_{ij} equal to zero. In terms of quantitative performance (AARD), at a temperature of 278.08 K, the PC-SAFT model exhibited a deviation of 14.91 %, while the Mod PR model showed a significantly higher deviation of 81.02 %. In this case, PC-SAFT demonstrated much superior performance, with significantly lower deviations, whereas Mod PR proved inadequate for predicting behavior at lower temperatures, highlighting its limitations in modeling. At 283.11 K, PC-SAFT maintained a reasonable deviation of 16.45 %, while Mod PR exhibited an extremely high deviation of 98.99 %, confirming the persistent performance gap between the models. Although the deviation of PC-SAFT increased with rising temperature, it remained the more accurate model.



Figure 4.16: Water Content in Ethane at Temperature 278.08 K, 283.11 K, 293.11 K and 298.11 K in Hydrate-Vapor Equilibrium; (...) Mod PR, (-.-) PC-SAFT; Experimental Data: 278.08 K (\blacktriangle), 283.11 K (\bigstar), 293.11 K (\bigstar), and 298.11 K (\bigstar) [4].

At 293.11 K, PC-SAFT continued to show consistent performance, with a deviation of 17.54 %, while PR Mod reached 123.62 %, indicating increasing difficulties in predicting water content at higher temperatures. Finally, at 298.11 K, PC-SAFT exhibited a reduced deviation of 7.61 %, suggesting improvement, whereas PR Mod maintained a high deviation of 119.27 %, further emphasizing its limitations. These results confirm the superiority of PC-SAFT under all analyzed conditions, with more robust performance and better accuracy in predicting water content in the hydratevapor equilibrium for the $C_2H_6+H_2O$ system. It can also be observed that, for ethane in equilibrium with hydrates, the increase in pressure does not significantly impact the gas's ability to dissolve water, indicating a weak dependence of solubility on pressure [4], and in that context the PC-SAFT was capable of predicting that behaviour with more precision than Mod PR. The presented results are predictive, with no direct correlation to experimental data. Furthermore, the parameters, especially those of PC-SAFT, were estimated under conditions different from those applied in this analysis.

4.4.1 Phase Diagram for the C_2H_6 and Water System

Figure 4.17 presents the phase diagram for the $C_2H_6+H_2O$ system, showing the hydrate dissociation conditions as a function of temperature and pressure for different water contents (352 ppm, 453 ppm, 501 ppm, and 564 ppm). The results simulated using the Modified Peng-Robinson (Mod PR), PC-SAFT, and PVTsim[®] models were compared with experimental data obtained by CHAPOY <u>et al.</u> (2003) and SONG and KOBAYASHI (1994). The evaluated models exhibited distinct behaviors in predicting the hydrate dissociation conditions for the analyzed system. The Modified PR model tended to underestimate the experimental data, indicating difficulties in capturing the system's behavior. On the other hand, the PC-SAFT model showed a closer fit to the experimental data, standing out as the most accurate model, especially for water contents above 400 ppm. Meanwhile, PVTsim[®] produced competitive results, with good agreement for higher water contents but deviated from the experimental data under conditions of lower water content.



Figure 4.17: Dissociation Conditions for Ethane Hydrate; (-.-) Mod PR, (- -) PC-SAFT, (...) PVTsim^(R); Experimental Data: (\triangleright), (\blacksquare), and (\blacklozenge) [4]; (\blacklozenge) [5].

The decrease in water content shifted the dissociation curves to lower temperatures at a given pressure, consistent with the trend observed experimentally. At lower water contents (352 ppm), the model predictions showed minor deviations from the experimental data, while higher water contents (564 ppm) resulted in greater accuracy in predictions, reflecting the challenge of modeling system behavior with lower content of water in the vapor phase. Compared to the experimental data, the PC-SAFT and PVTsim[®] models aligned reasonably well under specific conditions, but PC-SAFT demonstrated greater consistency across the entire range of temperature and pressure. The Modified PR model, on the other hand, exhibited larger deviations, highlighting its limitations in accurately modeling the interactions between ethane and water.

4.5 Water Content for the CO₂ and Water System in Gas-Dominated Conditions

Figure 4.18 presents the calculation of moisture content in hydrate-vapor equilibrium (HVE) for the CO_2+H_2O system, evaluating the performance of the PC-SAFT and Modified Peng-Robinson (PR Mod) models at different pressures (6.9 bar, 13.8 bar, 20.7 bar, and 34.5 bar). The results were compared with experimental data obtained by SONG and KOBAYASHI (1987), and the average absolute relative deviations (AARD%) were analyzed for each pressure condition. These results use modified PR parameters presented in Chapter 3 including k_{ij} , PC-SAFT parameters estimated as presented in Section 4.2 with k_{ij} equal to zero where the cross-association scheme for CO₂ was not considered.



Figure 4.18: Water Content in Carbon Dioxide at Pressure 6.9 bar, 13.8 bar, 20.7 bar and 34.5 bar in Hydrate-Vapor Equilibrium; (...) Mod PR, (- -) PC-SAFT; Experimental Data: 6.9 bar (\blacktriangle), 13.8 bar (\bigstar), 20.7 bar (\bigstar), and 34.5 bar (\bigstar) [6]

At a pressure of 6.9 bar, the PR Mod model exhibited significantly better performance, with an AARD of 2.36 %, while PC-SAFT showed a larger deviation of 25.69 %, indicating difficulties in describing the behavior of water in equilibrium with CO₂ at lower pressures. At 13.8 bar, both models experienced an increase in deviations, with PR Mod maintaining higher accuracy (11.18 %) compared to PC-SAFT (24.48 %). However, a worsening trend for PR Mod was observed with increasing pressure, while PC-SAFT exhibited more consistent behavior despite the high deviations.

At 20.7 bar, PC-SAFT began to outperform PR Mod, with deviations of 17.10 % compared to 34.43 %, suggesting that PC-SAFT is better suited for intermediate pressures, where specific interactions between CO₂ and H₂O become more relevant. Finally, at 34.5 bar, both models exhibited high deviations, with 27.33 % for PC-SAFT and 37.34 % for PR Mod, but PC-SAFT maintained slightly better performance, indicating greater robustness under high-pressure conditions where non-ideal behavior becomes more pronounced. The results indicate that model performance strongly depends on pressure. At lower pressures (6.9 and 13.8 bar), PR Mod stood out, providing more accurate predictions with reduced deviations, which can be attributed to its simplicity and good fit for systems where molecular interactions are less significant. However, as pressure increases (20.7 and 34.5 bar), PC-SAFT began to perform better, reflecting its ability to handle more complex interactions and non-ideal effects present in systems with higher density and water activity.

Although PC-SAFT exhibited higher deviations at lower pressures, it proved more robust at intermediate and high pressures, making it more suitable for extreme conditions where precision is critical. On the other hand, PR Mod can be considered a viable alternative for quick estimates at lower pressures but shows significant limitations under more severe conditions. It can also be observed that, for CO_2 in equilibrium with hydrates, the increase in pressure impacts the gas's ability to dissolve water, and both models are able to capture this behavior. The presented results are predictive, with no direct correlation to experimental data. Furthermore, the parameters, especially those of PC-SAFT for the pure components, were estimated under conditions different from those applied in this analysis.

4.5.1 Phase Diagram for the CO₂ and Water System

Figure 4.19 presents the phase diagram for the $CO_2 + H_2O$ system, showing hydrate dissociation conditions as a function of temperature and pressure for different water contents (119.4 ppm, 220.1 ppm, and 379.4 ppm). The results simulated by the Modified Peng-Robinson (PR Mod), PC-SAFT, and PVTsim[®] models were compared with experimental data from SONG and KOBAYASHI (1987). The results showed that the Modified PR and PC-SAFT models provided more conservative predictions, systematically underestimating the experimental data at higher and intermediate pressures, suggesting limitations in the accurate description of molecular interactions between CO_2 and H_2O by both models. On the other hand, they showed better adherence to experimental data at intermediate temperatures. PVTsim[®] had an intermediate performance, closely matching experimental data at lower water content (119.4 ppm) and higher water content (379.4 ppm), but deviating at intermediate concentrations.



Figure 4.19: Dissociation Conditions for Carbon Dioxide Hydrate; (-.-) Mod PR, (-.) PC-SAFT, (...) PVTsim[®]; Experimental Data: (+), (>), and (\bullet) [6].

The decrease in water content shifted the dissociation curves to lower temperatures at a given pressure, in agreement with the experimental data. At low water content (119.4 ppm), the models showed more variation from the experimental data, suggesting sensitivity to non-ideal effects under these conditions. For higher concentrations (220.1 ppm and 379.4 ppm), the PVTsim[®] model performed better, while the PR Mod and PC-SAFT models continued to exhibit more significant deviations.

PC-SAFT and PR Mod showed more consistency across the entire range of temperatures and pressures analyzed, while PVTsim[®] showed mixed results, with higher accuracy at lower water contents but deviating at higher concentrations, which may limit its application in systems with high water activity.

The results indicate that model prediction varies significantly with water content and temperature. PC-SAFT and PR Mod proved to be more consistent, especially for predictions at higher water concentrations and higher pressures, making them recommended for applications requiring greater accuracy. PVTsim[®] demonstrated potential for quick predictions in systems with lower water content but showed limitations under more complex conditions.

Chapter 5

Conclusions

This dissertation comprehensively explored hydrate formation in gas-dominated systems using a robust thermodynamic model integrating the PC-SAFT and modified Peng-Robinson equations of state. A multiphase flash algorithm was successfully implemented and applied to gas-dominant systems. Stability analysis and phase equilibrium predictions were consistent with experimental data, even under extreme temperature conditions (below 260 K) and pressure conditions (above 10 bar), such as those encountered in offshore environments, while also enabling the calculation of water content in gas under similar scenarios.

The proposed multiphase flash algorithm remains robust for both phase equilibrium calculations and the determination of water content in gas, with the presence of hydrates, in gas-dominated systems. Its flexibility allows for changing the specified variables, facilitating the computation of variables of interest as needed. Additionally, the stability analysis integrated into the algorithm is a valuable tool, as it indicates the thermodynamic conditions under which the aqueous phase no longer appears, allowing the identification of the transition from a three-phase equilibrium to a two-phase equilibrium, such as Hydrate-Vapor equilibrium. This feature is particularly useful for predicting hydrate formation limits and assisting in the operational control of industrial processes.

Furthermore, three equations of state were compared: the modified Peng-Robinson with parameters from the literature, PC-SAFT with fine-tuned parameters, and the default PVTsim[®] model. The results showed good agreement with the available experimental data, demonstrating the competitive performance of the proposed methodology compared to commercial software. Notably, the PC-SAFT model exhibited promising predictive capability, as only pure-component parameters were estimated, with binary interaction parameters set to zero.

Experimental data were found for methane, ethane, and carbon dioxide, with methane showing good data coverage at low and intermediate pressures across a wide temperature range. However, additional data in the pressure range of 0.5 to 2.5 MPa at temperatures below 250 K for carbon dioxide, in the pressure range of 1.5 to 3 MPa at temperatures below 270 K for ethane, and in the pressure range of 1 to 8 MPa at temperatures below 273 K for methane would be desirable to improve model validation and fine-tuning for industrial applications. Additionally, experimental data for carbon dioxide and methane mixtures in different proportions would also be important for enhancing model calibration.

The industrial relevance of this study is significant, as it provides a valuable tool for predicting hydrate formation conditions and mitigating risks related to pipeline blockages in oil and gas exploration operations. Moreover, by accurately predicting the water content given thermodynamic conditions and determining whether hydrate deposition occurs under such conditions, the industry can implement or dismiss mitigation measures with reasonable confidence, such as installing a dehydration unit.

5.1 Suggestions for Future Work

Suggestions for future work include expanding the experimental database by conducting new studies on gas-dominant systems with varied hydrocarbon and contaminant compositions, such as H_2S and CO_2 , to validate and improve the proposed models.

During this study, limitations were observed in the models related to the ability to predict water content in liquid CO_2 . The PC-SAFT equation of state showed difficulties in capturing the equilibrium behavior of $CO_2(L)$ +H at low water content. This issue may be linked to the molecular framework adopted for carbon dioxide. As an acid gas, CO_2 interacts significantly with water molecules, including hydrogen bonds and Lewis acid-base interactions. Incorporating cross-associations between CO₂ and H₂O into the PC-SAFT model could theoretically enhance predictions for the water content in $CO_2(L) + H$ equilibrium [76]. However, the strong interactions between CO_2 and H_2O , driven by the quadrupolarity of CO_2 and the high association capacity of H_2O , make this system highly non-ideal and challenging to model. Using SAFT variants, such as tPC-SAFT, may improve performance for systems with more pronounced polar interactions [77]. In the context of offshore exploration in Brazil, particularly in Pre-Salt fields where CO_2 concentrations can reach up to 80% [25], a deeper understanding of the $H_2O - CO_2$ system is crucial. This applies especially to the $CO_2(L) + H$ equilibrium region, which is relevant to natural gas dehydration and carbon capture and storage (CCUS) processes [43].

Additionally, exploring alternative methods for calculating the Langmuir constant for the solid phase could bring significant advancements. Alternative approaches, using empirical expressions to improve the intermolecular interactions between the guest and water, could be investigated to enhance prediction accuracy for equilibrium behavior in multiphase systems. A promising strategy would integrate quantum and classical methods, employing Density Functional Theory (DFT) to examine molecular interactions and derive fundamental thermodynamic parameters directly from quantum calculations. This approach could provide Langmuir coefficients through *ab initio* calculations, capturing specific interactions between guest and host molecules with better acuracy. These calculations could also incorporate classical models, such as PC-SAFT or tPC-SAFT, bridging microscopic and macroscopic scales.

Finally, another suggestion is to incorporate the PShift model [18] into the algorithm used in this study. This model has potential to improve volumetric and equilibrium property calculations, particularly under high-pressure and low-temperature conditions. Integrating PShift into the multiphase flash algorithm, along with stability analysis, could enhance robustness and reliability for industrial applications.

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