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Comparison of Hydrates Formation Modeling Software Performance

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Abstract

Predicting hydrate stability/formation conditions is crucial for the oil and gas industry mainly to avoid pipelines blockage during oil and gas transportation and supplying. Additionally, exploitation methods of the natural gas and CO₂ storage in hydrates have started gaining attention recently. Thus, understanding under what conditions hydrates are stable or can be stabilized is very important. Based on that, accurate knowledge of hydrate modeling in the presence of salts, inhibitors and non-ideal components is a main key in all related sectors.

In the first part of this work, various approaches/models available in the literature and in the industry to describe hydrates thermodynamic behavior are presented and studied in detail so that the differences in stability, solid solution theory of Van der Waals and Platteeuw and the specific thermodynamic models representing all phases that co-exist (ice, water, solid CO₂) adopted in each approach are well understood.

Subsequently, the accuracy of the approaches describing the phase equilibria of gas hydrates in the presence of CO₂ components, high/low concentration of aqueous salt(s) and/or high/low concentration of inhibitor(s) is evaluated. The approaches studied and tested are implemented in four well known commercial software packages extensively used in the industry, that hold the following industrial/developing name and the corresponding (approach): HydraFlash/HydraFact (HF, HF72), MultiFlash/KBC (MF(CPA)/MF(RKSA), CSMGem (CSMGem), CSMHyd (CSMHyd).

The accuracy comparison is run against a large database of experimentally measured hydrate dissociation conditions which has been collected from papers that appeared in the literature between 2015-2019. The collected experimental data has been reproduced using all six approaches and the obtained results have been utilized to evaluate the accuracy of each method as a function of the temperature and pressure of the system.

The results obtained are analyzed in detail and the reasons explaining the accuracy/deviations of each approach are presented. It has been found that the accuracy of the six studied approaches are ordered as follows (from most to less accurate): HF > HF72 > MF CPA > MF RKSA > CSMGem > CSMHyd.

This copy is a Preliminary Version

Dedication

Dedicated to my Father Ali (1965-2003).

Acknowledgments

This thesis is submitted in partial fulfilment of the requirements for the MSc. degree at Technical University of Crete. This work has been conducted with collaboration of Heriot Watt University, HydraFact Company and National Technical University of Athens, under the supervision of Professor Bahman Tohidi and Professor Vassilis Gaganis. The project has no fund or grants by any of the institution or supervisor mentioned. However, a six-month free license for HydraFLASH Software was provided by HydraFact Company, MultiFlash license from technical university of Crete and both CSM software by Dr. Dimitris Marinakis.

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A thesis submitted to the committee members

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Chapter 1

1 Introduction

This chapter serves several purposes: 1. an introduction to clathrate hydrates, 2. current topics in hydrate research/technological applications, 3. an introduction to the thermodynamic and kinetic modeling of clathrate hydrates, and 4. an indication of what this work encompasses with respect to clathrate hydrates. This chapter will provide background so that following chapters can be better understood.

Gas hydrates (also known as clathrate hydrates) are solid inclusion compounds that are formed when water and gas come into contact at high pressures and low temperatures. This host-guest system comprises a host lattice of hydrogen-bonded water molecules that form cages, which encapsulate guest gas molecules such as methane, carbon dioxide, and propane (Sloan ED 2008).

Sir Humphry Davy (H. 1811) first discovered gas hydrates in 1810 when he noticed that a solid was formed from a solution of chlorine gas (then known as oxymuriatic gas) and water above the ice point. The discovery may have even preceded Davy, as in 1778 Priestley discovered compounds (formed from freezing SO_2 in water) that may have been clathrate hydrates, but the lack of adequate documentation makes this earlier discovery uncertain (Sloan ED 2008).

Gas hydrates were not considered to have any practical relevance until 1934, when Hammer Schmidt discovered that gas hydrates rather than ice were responsible for plugging gas transmission lines in Canada (EG 1934.). Gas hydrates still continue to plague the oil and gas industry, as they cause a severe risk of blockages in oil and gas pipelines, both onshore and offshore. Deep-water offshore oil fields have enhanced high pressure and low temperature environments; thus, the risk of gas hydrate blockages in pipeline and offshore facilities is extreme. As such, gas hydrates are the primary problem for flow assurance, the field concerned with ensuring continuous flow of fluids in oil/gas flow lines and facilities.

Gas hydrate formation is also a key issue in deep-water oil/gas production from a safety perspective. As recently witnessed in 2010, gas hydrates were a major problem in the containment of the oil leak following the deep-water oil/gas well blowout of the Macondo well in the Gulf of Mexico. At the water depths where the oil leak was located, the temperature and pressure conditions were readily favorable for the formation of gas hydrates from the rising oil/gas plume. In fact, gas hydrate formation was the cause for the failure of a 100-ton containment structure following the Macondo well blowout in the Gulf of Mexico. As such, subsequent containment of the oil leak required incorporation of effective hydrate mitigation strategies to prevent hydrate formation.

Although gas hydrates are considered a nuisance when they occur in oil/gas flow lines, they are considered a potential asset when present in large natural deposits in arctic regions under the permafrost and in oceanic sediments along the continental margins. The global estimates of the amount of energy (methane gas) trapped within natural gas hydrate deposits varies widely, but even the most conservative estimates place the amount of energy in hydrated deposits to be twice

that of all fossil fuel reserves available worldwide; upper estimates of gas hydrate deposits are orders of magnitude greater than those for natural gas reserves (Paull C 2010.).

According to the recent National Research Council report on methane hydrates (Paull C 2010.) , there are no fundamental technological hurdles to recovering energy from these natural deposits , although more research needs to be performed to determine the environmental impact of such exploration.

1.1 Gas Hydrate Technological Applications

Other technological applications of gas hydrates include storage of natural gas and hydrogen (H₂). The ability to store natural gas in the form of gas hydrate pellets is appealing, particularly for stranded gas applications where the produced gas is too small to justify building a liquefied natural gas plant and production is too far away from a pipeline (Andersson V 2000) (M. M. Gudmundsson JS 2002). The storage and transportation of natural gas hydrates are near commercialization; current work focuses on development and optimization for efficient production of large volumes/scale-up of gas hydrate pellets (Watanabe S 2008). Further details on the important lessons learned and heuristics for gas hydrates in energy applications, including flow assurance, energy production, and natural gas storage, are provided below.

1.2 Energy Storage in Gas Hydrates

Energy storage in gas hydrates presents an attractive solution to the transportation of stranded gas in hydrated form or to provide fuel to ships, with hydrate requiring a low-storage space and low-pressures. Methane hydrate has an energy density equivalent to a highly compressed gas, but is less energy dense than liquefied natural gas (LNG). Gudmundsson and Borrehaug (Gudmundsson JS June 2-6.1996) proposed to ship natural gas in hydrated form, rather than in LNG tankers, suggesting the economics were favorable. This basic concept has been extended by researchers from Mitsui Shipbuilding in conjunction with the Japanese Maritime Research Institute (Takaoki T June 13-16) . The hydrated gas is stored in pellet form at low temperatures. The stability of these pellets can be enhanced by exploiting the concept of anomalous preservation first reported by Stern and coworkers (Stern LA 2001).

Efforts to develop clathrate hydrate materials for hydrogen storage followed the reports that hydrogen could be stored in pure hydrogen hydrate at high-pressures (Mao WL n.d.) And stored at lower pressures by adding THF as a promoter molecule (Florusse LJ n.d.). The key challenge for hydrogen storage in hydrates is to balance the storage capacity with the requirement for mild pressure and temperature conditions for storage. The development of fuel storage materials (both for natural gas and hydrogen) requires an improved understanding of the structure-stability relations of these host-guest systems.

1.3 Energy Recovery and Production of Natural Hydrates

Gas hydrates occur naturally within and under permafrost in arctic regions and within ocean sediments (Sloan ED 2008). The most recent estimates of the total amount of methane (STP) in these hydrated gas deposits vary from 0.2×10^{15} to 12×10^{16} m³. Despite this wide range of estimated

gas, all estimates are significant when compared to evaluations of the conventional gas reserve of $0.15 \times 10^{15} \text{ m}^3$ methane (STP) (M. 2000). In the United States the mean hydrate value indicates 300 times more hydrated gas than the gas in the total remaining recoverable conventional reserves. Hydrate reservoirs are considered a substantial future energy resource due to the large amount of hydrated gas in these deposits, coupled with hydrates concentrating methane (at STP) by as much as a factor of 164 and requiring less than 15% of the recovered energy for dissociation. However, energy recovery is an engineering challenge.

Three general heuristics (Trehu AM 2006) for naturally occurring ocean hydrates are:

1. Water depths of 300-800 m (depending on the local bottom water temperature) are sufficient to stabilize the upper hydrate boundary.
2. Biogenic hydrates predominate, with only a few sites comprising thermogenic hydrates (containing CH_4 and higher hydrocarbons), such as in the Gulf of Mexico, Cascadia and in the Caspian Sea. These thermo genic deposits tend to comprise large accumulations near the sea floor.
3. Hydrates are typically found where organic carbon accumulates rapidly, mainly in continental shelves and enclosed seas. These are biogenic hydrates (containing CH_4 , formed from bacterial methanogenesis). More details of the mechanism of generation of Bio & thermogenic gas in (Sloan ED 2008)

1.4 Gas and Oil Production and Transportation (Flow Assurance)

Gas and oil production and transportation in subsea flow lines is moving to deeper water depths (>6000 ft), hence more extreme temperature and pressure conditions. These conditions are highly favorable for hydrates to form within the flow line, which can result in blockages and as a consequence economic loss accompanied by ecological and safety risks (Sloan ED 2008). The typical method used to prevent hydrate formation within subsea flow lines is to add a thermodynamic inhibitor (such as methanol or monoethylene glycol), which shifts the hydrate formation conditions to lower temperatures and/or higher pressure (Sloan ED 2008). . Figure 1 provides a visual description of thermodynamic inhibitor effect on shifting thermodynamic conditions stability phase of hydrates. Other thermodynamic methods of avoiding hydrate formation include heating the system to above the hydrate formation conditions, insulating the flow line, separating the free water and drying the gas.

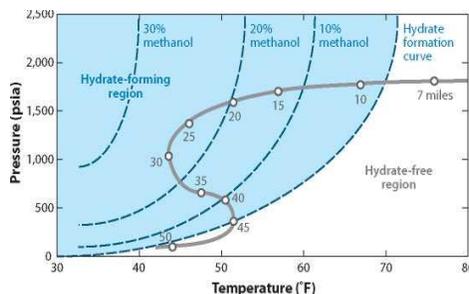


Figure 1 Pressure and temperature conditions of in a subsea pipeline (Sloan ED 2008).

However, in many deep-water production scenarios, thermodynamic inhibition can become uneconomical and even prohibitive due to the high concentrations of inhibitor required. Therefore, flow assurance is progressively moving away from avoidance (thermodynamic control) of hydrate formation toward risk management (kinetic control) which may allow hydrates to form, while preventing a hydrate blockage (Sloan ED 2008).

Hydrate plugs are not typically formed during normal flow line operation by design. However, plugs can occur due to the following abnormal flow line operations:

1. When the water phase is uninhibited as a result of inhibitor injection failure, dehydrator failure, or the production of excess water,
2. During startup following an emergency shut-in performed due to system failure or adverse weather conditions, such as a hurricane, or
3. When water-wet gas expands rapidly through a valve, orifice or other restriction, resulting in significant Joule- Thomson cooling at under-inhibited conditions.

New technologies currently (Sloan ED 2008) being developed to control hydrate formation within deep-water flowlines during normal and abnormal operations include:

1. The addition of low dosage hydrate inhibitors (LDHIs) that are effective at concentrations below about 1 wt. %.¹² There are two broad classes of LDHIs: kinetic hydrate inhibitors (KHIs) and antiagglomerants (AAs). KHIs (e.g. poly-N-vinyl-caprolactam) operate by delaying nucleation and/or crystal growth. AAs (e.g., quaternary ammonium salts) prevent hydrate crystals from agglomerating to form a blockage, by maintaining the hydrates in the form of a suspended slurry which allows fluid flow to occur unimpeded.
2. “Cold flow”, denotes the process, whereby hydrates could be pumped as a slurry through the flow line without the need for chemical inhibitors. Sintef-BP researchers have reported that the addition of water to a flow of dry hydrate results in the formation of further dry hydrate. It is suggested that capillary attractive forces between dry hydrates are low; hence, these particles should not agglomerate to form a plug. This economic technique of risk-management appears promising.
3. Hydrate plug remediation methods include depressurizing the line, injecting a thermodynamic inhibitor, or electrical heating. Plug dissociation occurs radially and dissociation times can be predicted using a Fourier’s Law model (e.g., CSMPlug). However, single-sided plug depressurization can be life-threatening due to the potential for a pressure- driven projectile and, therefore, safety should be a major consideration. Unlike one-sided dissociation, careful two-sided dissociation normally eliminates the concern of having a projectile in the pipeline.

The thermodynamics of hydrate formation is well-established, with a number of reliable and adequately accurate prediction programs available (e.g., HydraFlash, MultiFlash, CSMHyd, CSMGem) using different models. However, the time-dependent processes of hydrate formation and decomposition are still poorly understood. A major challenge is predicting the time required

for hydrate crystals to nucleate, grow, agglomerate and eventually form a hydrate plug in a transient, multiphase flow line.

Hydrate nucleation studies are particularly challenging due to the stochastic, microscopic nature of the nucleation process, which involves 10s to 1,000s of molecules. Nucleation and hydrate induction (formation) times are affected by a number of variables, including: apparatus geometry, surface area, water contaminants and history and the degree of agitation or turbulence. This makes it very difficult to transfer the results from one laboratory or flow loop facility to another. The question of transferability and scale-up to field conditions is even more daunting. Therefore, being able to predict when hydrates will nucleate and grow is a major challenge which is critical to assessing the risk of hydrate formation.

For hydrate formation in liquid hydrocarbon systems, fundamental understanding of the chemistry of the system (water- in-oil and oil-in-water emulsion chemistry and interfacial interactions) coupled with multiphase flow is needed. The phenomenon of hydrate particle agglomeration is key to determining the risk of hydrate plug formation.

1.5 Gas Hydrate Structure and Composition

1.5.1 Clathrate Hydrates

Clathrate hydrates are non-stoichiometric crystalline compounds that consist of a hydrogen bonded network of water molecules and enclathrated molecules. Davy (H. 1811) first observed clathrate hydrates in the chlorine + water system. It wasn't until 1934, however, that clathrate hydrates were extensively studied. Hammerschmidt (EG 1934.) Found that natural gas transport lines could be blocked by the formation of clathrate hydrates. This raised a lot of attention in the oil and gas industry, prompting more research to be performed on clathrate hydrates of natural gas. With the majority of research being done on clathrate hydrates of natural gas, clathrate hydrates are typically referred to as natural gas hydrates.

Natural gas hydrates are formed when natural gas is brought into contact with water, generally at low temperatures and high pressures. The guest molecules most common in natural gas systems are hydrocarbons ranging from methane to i-pentane. These gases make up greater than 98 mole percent of a typical natural gas in United States pipelines. Therefore, the majority of the experimental work performed in the last 70 years has been for hydrates of hydrocarbons ranging from methane to i-pentane (Sloan ED 2008).

There are three basic hydrate structures known to form from natural gases: structure I (sI), structure II (sII) and structure H (sH). The type of hydrate that forms depends on the size of the gas molecules included in the hydrate. In general, small molecules such as methane or ethane form sI hydrates as single guests, larger molecules such as propane and i-butane form sII hydrates, and even larger molecules such as i-pentane form sH hydrates in the presence of a small "help" molecule such as methane. When sI, sII and sH hydrate formers are in a mixture, it is not easy to generalize which hydrate structure will be present. However, the type of hydrate that forms will depend on the composition, temperature and pressure of the system (Sloan ED 2008).

The basic "building block" of each of these structures is the pentagonal dodecahedron, which is a 12-sided pentagonal faced polyhedral (5). There are twenty water molecules in this cage with the oxygen atoms at each vertex and the hydrogen atoms either chemically or hydrogen bonded between each oxygen atom. The bonds between the hydrogen and oxygen molecules essentially hold the cage together and the guest molecules serve to keep it from collapsing. Depending on what gases are present and ultimately which hydrate structure is formed; these basic cages stack to form more complex cages. For sI hydrates they form tetra decahedron cages that have 12 pentagonal and 2 hexagonal faces (5 6). For sII hydrates, hexadecachoron cages are formed; 12 pentagonal and 4 hexagonal faces (5 6). For sH hydrates, two new cages are formed which are, using the previous nomenclature for a cage, $4^35^66^3$ and $5^{12}6^8$. Figure 2 provides a visual description of each hydrate cage.

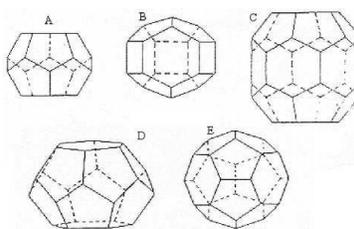


Figure 2 Cavities which combine to form different hydrate structures A) 5^{12} B) $4^35^66^3$ C) $5^{12}6^8$ D) $5^{12}6^2$ E) $5^{12}6^4$

A unit cell of a particular hydrate structure is specified by how the respective cages combine to form a periodic crystalline lattice. Figure 3 shows how the various cages are arranged to form a unit cell of each of the three most common structures.

For example, one-unit cell of sI hydrate contains 2 5^{12} cages and 6 $5^{12}6^2$ cages. Notice that the relative amount of small (5^{12}) cages varies within each hydrate structure. For instance, sI hydrates are comprised of one-quarter 5^{12} cages, sII hydrates are comprised of two-thirds and sH hydrates are comprised of one-half. Differences between the hydrate structures such as this play a major role in stability considerations.

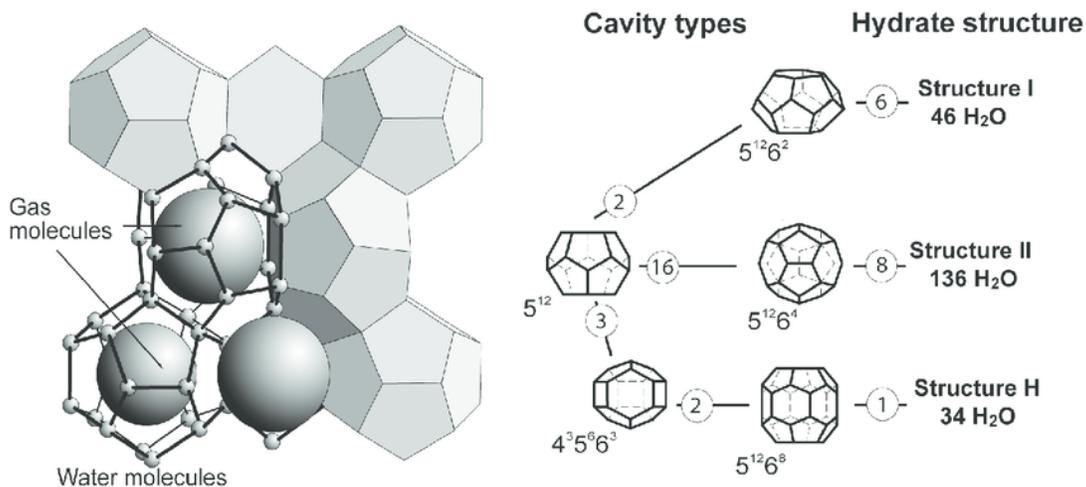


Figure 3 Combination of cages to form each hydrate structure

1.6 Main Points Describing the Importance of This Work for Oil and Gas Industry

Natural gas looks set to become the world's most important energy source within a decade. The market size for oil and gas pipeline construction experienced tremendous growth prior to the economic downturn in 2008. After faltering in 2009, demand for pipeline expansion and updating increased the following year as energy production grew. Natural gas hydrates are responsible for pipeline plugging and corrosion. Thus, handling the issue of the formation is a matter of vital importance for the industry. Based on that and in order to provide the optimal strategy in dealing with hydrate formation, it is of vital importance for the industry to have an understanding of the conditions that cause hydrate formation. In the other hand, in all the gas hydrate technological applications, it is clear that the paradigm is focusing on thermodynamics (time-independent properties) modeling and hydrate formation and dissociation properties. Improved understanding and control of the thermodynamics of these processes are key factors to advancing the technologies required in:

- Maintaining flow in pipelines by assessing the statics of hydrate formation, e.g. determining when a hydrate plug will occur.
- Accurately predicting the type of gas hydrates forms: Hydrate I, II or H as well as the complex phase transitions among the fluid and hydrate phases (e.g.: transition of hydrate structure II to I).
- Reducing operational costs (OPEX) for the industry by accurately predicting hydrate formation conditions as well as hydrate inhibition effect on hydrate formation condition such as: Methanol, ethanol, MEG, DEG and TEG.
- Gas recovery from hydrate deposits by assessing the techniques needed to dissociate and release the gas from the deposit at specific thermodynamic conditions.
- Assessing submarine hydrate dissolution rates and the impact of this dissociation to the environment.

In addition, the need of a reliable flow assurance engineering approach/tool will enable reservoir engineers as well as process engineers to optimize detailed field planning activities such as:

- Quantifying the risks and problems arising from hydrate formation.
- Life field study on inhibitor requirement and formulation of hydrate preventing strategies.

Chapter 2

2 Gibbs Energy Minimization and Stability Analysis

A clear understanding of the thermodynamic properties of gas hydrate systems is critical in all gas hydrate applications, from determining the temperature and pressure conditions at which a pipeline will be within the hydrate stability zone, to assessing the conditions necessary to dissociate a gas hydrate plug in a pipeline or a natural gas hydrate reservoir for energy production, to simply establishing the conditions at which a gas hydrate system can be synthesized in the laboratory. Gas hydrate stability depends on temperature, pressure, gas composition and condensed phase composition (including liquid hydrocarbon phase, salt content and chemical inhibitor concentration). Therefore, a method to calculate dissociation pressure and temperature and in particular hydrate properties at any pressure and temperature is desired. This chapter discusses the approach taken to perform these types of calculation using minimization of Gibbs energy of the system.

2.1 Essence of The Problem

We want to relate quantitatively the variables that describe the state of equilibrium of two or more homogeneous phases (intensive properties are everywhere the same) that are free to interchange energy and matter. We are concerned primarily with the intensive properties temperature, density, pressure and composition (mole fractions). We want to describe the state of two or more phases that are free to interact and that have reached a state of equilibrium. Then, given some of the equilibrium properties of the two phases, our task is to predict those that remain.

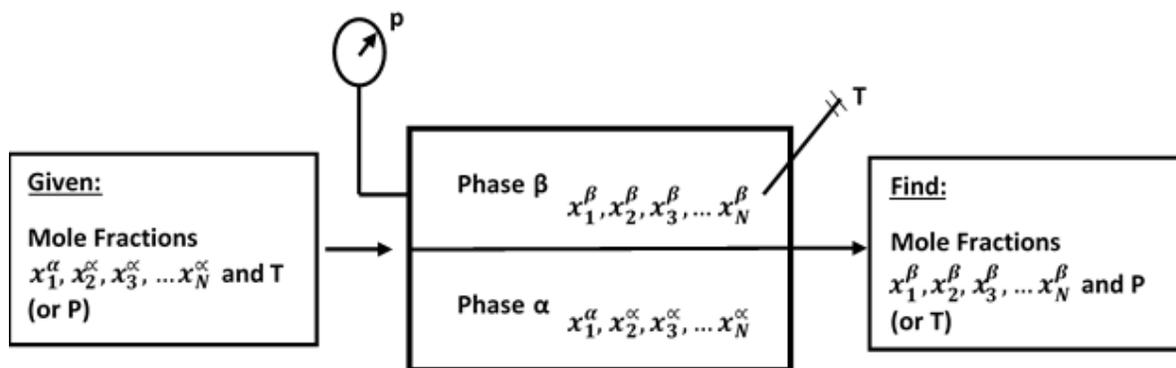


Figure 4 Problem Statement.

Our problem might be characterized by other combinations of known and unknown variables. The number of intensive properties that must be specified to fix unambiguously the state of equilibrium is given by the Gibbs phase rule. In the absence of chemical reactions, the phase rule is:

$$\text{Number of independent intensive properties} = \text{Number of components} - \text{Number of phases} + 2$$

The questions that may raise here:

- How shall we go about solving the problem illustrated in Fig. 4?

- What theoretical framework is available to give us a basis for finding a solution?

When this question is raised, we turn to thermodynamics.

Thermodynamics into Phase-Equilibrium Problems

- **Keyword: Abstraction** is describing a difficult real problem in abstract mathematical terms. It is sometimes possible to obtain a simple solution to the problem, not in immediate physical reality but in terms of mathematical quantities.
- **Role of thermodynamics:** Providing the mathematical language that enable us to obtain an abstract solution of the phase equilibria problem.

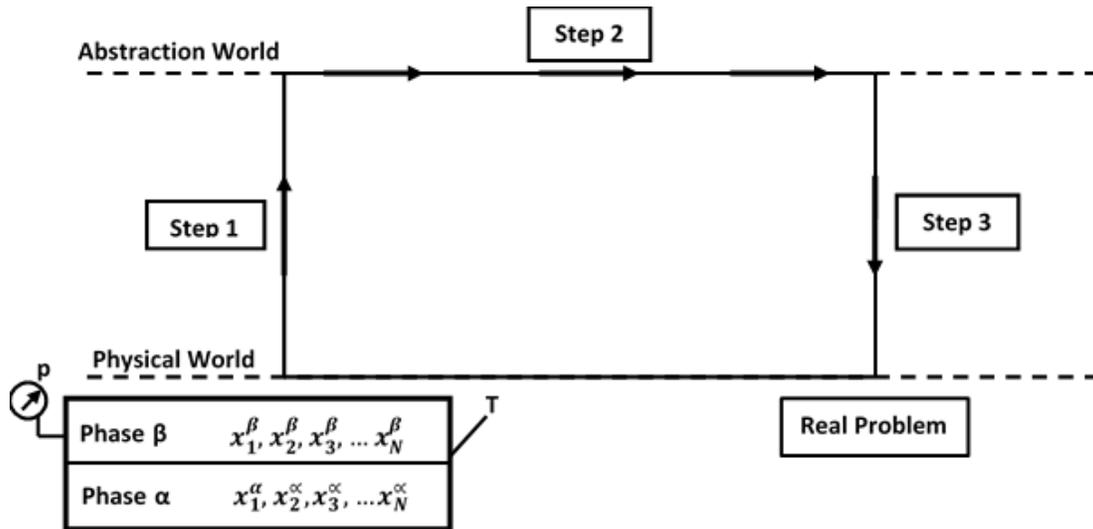


Figure 5 Three-step application of thermodynamics to phase-equilibrium problems.

The three step applications of thermodynamics to a real problem consists of indirect mental process. The indirect process first projects the problem to abstract world, then seeks a solution with that world and finally projects this solution back to Physical world.

2.2 Three-Step Application Procedure

Step 1: Translation of the Real Problem into an Abstract, Mathematical Problem

Main objective in this step is to define an appropriate and useful mathematical/thermodynamic function that define and characterize the system/problem so to facilitate Step 2. In our case (state of equilibrium), the profound insight of (Gibbs 1861) defined the chemical potential function which made it possible to achieve goal of Step 2. This function state that at equilibrium chemical potential of each component must be the same in every phase for each component as following

$$\mu_i^\alpha = \mu_i^\beta \quad (2.1)$$

Step 2: A Solution Is Found to the Mathematical Problem

Main objective in Step 2 is to solve the thermodynamics/mathematical constraint or equation that have been already defined in Step 1. The question that may rise here is how to correlate μ_i^α chemical potential to required quantitative data (P, T, x_i^α). The answer for this question is to rely on finding and establishing relationships between μ_i^α and P, T, x_i^α by using some auxiliary functions. This auxiliary function are fugacity's and activity coefficient by keeping in mind that this function does not solve the problem but make it easier & simpler to find a solution and they are easier to understand and be felt than abstract concept of chemical potential.

For example:
$$\mu_i^\alpha = \mu_i^\beta \quad (2.1)$$

$$\varphi_i y_i P = \gamma_i x_i f_i^0 \quad (2.2)$$

Where, in the vapor phase, y_i is the mole fraction and φ_i , is the fugacity coefficient, and in the liquid phase, x_i is the mole fraction, γ_i is the activity coefficient, and f_i^0 is the fugacity of component i at some fixed condition known as the standard state.

Equation 2.2 is more valuable for engineers but from thermodynamic point of view Eq 2. 2 is not more or less fundamental than Equation 2. 1. In addition, it includes 3 variables of our interest (y_i , x_i , P) where φ_i and γ_i are actually useful because they are numerical factors, frequently order of unity establishing connection between real mixture and thus by choice have be defined as ideal mixtures. However, we cannot assume an ideal behavior and we must establish two relationships for φ_i and γ_i where

$$\varphi_i = F_\varphi(T, P, y_1, y_2, \dots) \quad (2.3)$$

and
$$\gamma_i = F_\gamma(T, P, x_1, x_2, \dots) \quad (2.4)$$

where in following chapters, relationships of φ_i and γ_i will be discussed in detail.

Step 3: Translating Back the Mathematical Solution to A Real Physical Meaning

Due to limited information on the relation between the abstract chemical potential and the real experimental accessible quantities like temperature etc. classical thermodynamic cannot provide all necessary information about the system where this step includes additional constraints outside of the real meaning of classical thermodynamic that make the solution to sound and have a physical meaning. In case of phase equilibrium can be the material balance constraint or more precisely mass balance. Mass balance is satisfied by the usage of Well-known (Rachford (1952)).

Quick Summary

In order to formulate a phase equilibrium (Two phase or Multiphase) problem the steps below are followed:

1. Start by Gibbs equation that describe closed system at thermodynamic equilibrium (Eq. 2. 1)

2. Translate Gibbs equation of the real problem into an abstract mathematical problem using thermodynamics relationships and taking into consideration given information and required ones.
3. Correlate chemical potential μ_i to P, T using appropriate auxiliary equations for your case.
4. Add necessary constraints that make your problem physically valuable so to complete formulation of your problem.

Result: Thermodynamic equilibrium is formulated mathematically. Problem solved

2.3 Phase Equilibrium Criteria

Based on what we have discussed in section before and in order to calculate thermodynamic equilibrium for a closed system, two fundamental conditions must be met:

1. Equality of chemical potential of each component in each phase present.
2. Material balance is satisfied.

Where the first condition results from the Gibbs energy being at a minimum (Gibbs 1861). These conditions are commonly used in developing procedures for solving for thermodynamic equilibrium. The most common implementation of these conditions is for the two-phase system, vapor and liquid hydrocarbon, known as the VLE Flash. Where the requirement that the Gibbs energy of the system must be at a minimum, at a given temperature and pressure, is a statement of the second law of thermodynamics.

2.4 Phase Equilibria

In the following part we are going to look at phase equilibria problem from petroleum engineering (reservoir engineering) point of view. After that we are going to extend the basis of VLE two phase equilibria to Multiphase flash present implemented in hydrate modelling.

2.4.1 Vapor-Liquid Equilibria

As far as VLE is concerned, we can list a number of systems that are at the heart of petroleum fluid production that involve this phenomenon such as Separators, Reservoir, Pipelines, Wellbore, LNG Processing, NGL Processing, Storage, Oil and LNG Tankers.

Vapor/liquid equilibrium pertains to all aspects of petroleum production with which we are concerned. It is no wonder, then, that we devote a new module to the subject itself.

In a typical problem of liquid and vapor coexistence, we are usually required to know one or more of the following:

- The phase boundaries,
- The extent of each phase,
- The quality of each phase.

The main emphasis is on the quantitative prediction of the above. These three represent the three basic types of VLE problems. A more detailed description of each of them is given below.

2.4.1.1 Phase Boundary Determination Problem

These types of problems are either a bubble-point or a dew-point calculation. They are mathematically stated as follows:

- **Bubble-point T calculation:** Given liquid composition (x_i) and pressure (P), determine the equilibrium temperature (T),
- **Bubble-point P calculation:** Given liquid composition (x_i) and temperature (T), determine the equilibrium pressure (P),
- **Dew-point T calculation:** Given vapor composition (y_i) and pressure (P), determine the equilibrium temperature (T),
- **Dew-point P calculation:** Given vapor composition (y_i) and temperature (T), determine the equilibrium pressure (P).

2.4.1.2 Relative Phase Quantity Determination

In this type of problem, overall composition (z_i), pressure (P) and temperature (T) are given and the extent of the phases (molar fractions of gas and liquid) are required.

2.4.1.3 Phase Quality Determination

In this type of problem, overall composition (z_i), pressure (P), and temperature (T) are given and the composition of the liquid and vapor phases is required.

Problems of types 5.1.2 and 5.1.3 are collectively referred to as *flash calculation* problems. All three are problems that we encounter in production & reservoir operations as petroleum engineers. Our focus now is on solving these sorts of problems. We want to use a predictive approach to do so but One of the most difficult aspects of making VLE calculations is knowing whether a mixture will actually split into two (or more) phases at the specified pressure and temperature. Traditionally, this problem has been solved either by conducting a two-phase flash or by making a saturation-pressure calculation. Both methods are expensive and not entirely reliable. In 1982, (M. Michelsen (1982a)), (M. Michelsen (1982b)) showed how the Gibbs tangent-plane criterion could be used to establish the thermodynamic stability of a phase (whether a given composition has a lower energy remaining as a single phase (stable) or whether the mixture Gibbs energy will decrease by splitting the mixture into two or more phases (unstable)). (Baker (1982)) Shows graphically how the Gibbs tangent-plane criterion is used to establish phase stability of simple binary systems and (M. Michelsen (1982a)) gives an algorithm to establish phase stability numerically. This issue is going to be discussed later on. The algorithms presented in this section assume that a mathematical solution to the two-phase problem exists: either a solution yielding equilibrium phase compositions or a “trivial” solution. Even when the results appear physically consistent, a rigorous check of the solution with the phase-stability test (discussed latter) may be required. Alternatively, defining the phase stability before a two- phase flash calculation is made improves the reliability of the flash results but adds computations.

However, mathematically/thermodynamically, the two-phase flash calculation can be solved by either

1. Satisfying the equal-fugacity (alternatively equality of chemical potential of each component in each phase present and explained in section below) and material-balance constraints with a successive-substitution or Newton-Raphson algorithm.
2. Minimizing the mixture Gibbs free energy function.

2.4.1.4 Criteria for Chemical Equilibria in Terms of Fugacity

The concept of fugacity works so well because the criterion for chemical equilibria is just as simple as that using chemical potential (Gibbs equation mentioned in Step 1 above). To derive this relationship for fugacity, we begin by introducing Gibbs equation mentioned in step 1 and equating the chemical potentials of phases α and β :

$$\mu_i^\alpha = \mu_i^\beta \quad \text{Step 1}$$

So far, this analysis is relatively straightforward. G. N. Lewis had tremendous insight and inductively defined a new thermodynamic property, the fugacity, f ,

$$\mu_i - \mu_i^0 = RT \ln \left[\frac{\hat{f}_i}{f_i^0} \right] \quad (2.5)$$

Since energies never have absolute values, we need a reference state for chemical potential energy. The reference state is indicated by a superscript “o”. In choosing a reference state, we must specify the appropriate number of thermodynamic properties as prescribed by the state postulate; the rest of the properties of the reference state are then constrained. The reference chemical potential, μ_i^0 is the chemical potential at the reference pressure, P^0 and at **the same temperature as the chemical potential of interest**, T . Accordingly, fugacity has units of pressure. In this sense fugacity can be thought of as a “corrected pressure.” In fact, fugacity can roughly be translated from Latin as “**the tendency to escape.**” However, the concept of fugacity goes beyond gases. This defining equation is valid for an isothermal change from the reference state chemical potential to that of the system for all real species. **Lewis did not restrict the fugacity to the gas phase! It applies to liquid or solids as well.**

The definition above is not complete. The reference state is arbitrary; we are free to choose the most convenient reference state imaginable; however, both μ^0 and f^0 depend on the single choice of reference state and may not be chosen independently. Let’s consider a limiting condition to complete the definition. As the pressure goes to zero, all gases behave ideally; consequently, we define

$$\lim_{P \rightarrow 0} \left(\frac{\widehat{f}_i}{p_i} \right) = 1 \quad (\text{ideal gas}) \quad (2.6)$$

however, by replacing Eq. (2.5) into Gibbs Equation of equilibrium (Step 1)

Applying mathematical relationships and arranging we will obtain

$$\mu_i^{\alpha,o} - \mu_i^{\beta,o} = RT \ln \left[\frac{\widehat{f}_i^\alpha}{f_i^{\alpha,o}} \right] + RT \ln \left[\frac{\widehat{f}_i^\beta}{f_i^{\beta,o}} \right] \quad (2.8)$$

$$\mu_i^{\alpha,o} + RT \ln \left[\frac{\widehat{f}_i^\alpha}{f_i^{\alpha,o}} \right] = \mu_i^{\beta,o} + RT \ln \left[\frac{\widehat{f}_i^\beta}{f_i^{\beta,o}} \right] \quad (2.7)$$

The first three terms are just a restatement of Equation (2. 5); hence the remaining term must be equal to zero, that is,

$$0 = RT \ln \left[\frac{\widehat{f}_i^\beta}{\widehat{f}_i^\alpha} \right] \quad (2.9)$$

or
$$\widehat{f}_i^\alpha = \widehat{f}_i^\beta \quad (2.10)$$

Equation (2.10) forms the criterion for chemical equilibrium in terms of fugacity. It is just as simple as that for chemical potential. Fugacity is also mathematically much better behaved and valuable for engineering and computer implementation.

Thus, in practice, we can replace Equation (2. 1) with Equation (2. 10) in defining our criteria for equilibrium. In other words, in the followed procedure for any phase equilibria problem step 2 is where the chemical potential or Gibbs energy is reformulated using auxiliary equation so to be dependent on the required information (e.g. P, T, xi) and thus

$$\cancel{\mu_i^\alpha} = \cancel{\mu_i^\beta} \quad \widehat{f}_i^\alpha = \widehat{f}_i^\beta \quad \text{for chemical equilibrium}$$

The way of obtaining fugacity is discussed in the following chapters.

2.4.1.5 Fugacity Coefficient

Recalling Eq (2.6) as the pressure goes to zero, all gases behave ideally and the limit of fugacity to partial pressure equal to unity. Based on that we can define fugacity coefficient as following:

$$\widehat{\varphi}_i \equiv \frac{\widehat{f}_i}{p_{i,sys}} = \frac{\widehat{f}_i}{y_i P_{sys}} \quad (2.11)$$

The fugacity coefficient represents a dimensionless quantity that compares the fugacity of species

i to the partial pressure species i would have in the system as an ideal gas. A fugacity coefficient of one represents the case where attractive and repulsive forces balance and is usually indicative of an ideal gas. If $\varphi_i < 1$, the corrected pressure, or “tendency to escape,” is less than that for an ideal gas. In this case, attractive forces dominate the system behavior. Conversely, when $\varphi_i > 1$, repulsive forces are stronger. *Warning:* We define the fugacity coefficient relative to the system partial pressure, **not** the partial pressure of the reference state. A common mistake is to use the wrong pressure here.

2.4.1.6 Equilibrium and Equilibrium Ratios (K_i)

Consider a liquid-vapor in equilibrium. As we have discussed previously, a condition for equilibrium is that the chemical potential of each component in both phases are equal, thus:

$$\mu_i^\alpha = \mu_i^\beta$$

$$\widehat{f}_i^\alpha = \widehat{f}_i^\beta$$

This is, for a system to be in equilibrium, the fugacity of each component in each of the phases must be equal as well. The fugacity of a component in a mixture can be expressed in terms of the fugacity coefficient. Therefore, the fugacity of a component in either phase can be written as:

$$f_i^\beta = y_i \phi_i^\beta P \quad (2.12)$$

and

$$f_i^\alpha = x_i \phi_i^\alpha P \quad (2.13)$$

Now considering for liquid -vapor in equilibrium β represent the vapor phase (V) and α the liquid phase one (L) and introducing Eq. (2. 12) and Eq. (2. 13) into fugacity equality condition of equilibrium

$$y_i \phi_i^V P = x_i \phi_i^L P \quad (2.14)$$

This equilibrium condition can be written in terms of the equilibrium ratio K_i to have:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (2.15)$$

2.4.1.7 Mass Balance

For a system with C components and π possible phases, the following mass balance must be satisfied for each component:

$$\sum_{k=1}^{\pi} \alpha_k x_{ik} = z_i \quad (2.16)$$

$$i = 1, \dots, C$$

where a_k is the normalized molar amount of phase k (i.e. phase fraction) and x_{ik} is the mole fraction of component i in phase k . We can define a reference phase, r , with the requirement that it must be present at equilibrium (e.g. Liquid hydrocarbon in VLE). In this case, Equation 2.1 can be written as

$$a_r x_{ir} + \sum_{\substack{k=1 \\ k \neq r}}^{\pi} \alpha_k x_{ik} = z_i \quad (2.17)$$

$$i = 1, \dots, C$$

the following constraints are imposed on Eq. (2. 17)

$$\alpha_r = 1 - \sum_{\substack{k=1 \\ k \neq r}}^{\pi} \alpha_k \quad (2.18a)$$

$$\& \quad \sum_{i=1}^c x_{ik} = 1 \quad (2.18b)$$

$$k = 1, \dots, \pi$$

Equation (2. 17), with constraints (2. 18a) which state that all mass fractions of phases present sum up to unity and (2. 18b) a constraint that mole fractions in k phase must satisfy by add up to unity also, these two constraints are necessary for a closed system in order for the mass balance to be respected. After defining the concept of material balance and necessary constraint, let's implement that for VLE problem which is typical in petroleum engineering.

As we have defined before β represent the vapor phase (V) and α the liquid phase one (L). Additionally, x_i , y_i , z_i mole fraction in liquid vapor phase and original feed respectively. Defining Liquid hydrocarbon as a reference phase since we know that liquid phase is present at equilibrium and implementing Equation 2. 17 give us:

$$x_i \alpha + y_i \beta = z_i \quad i = 1, \dots, C \quad (2.19)$$

implying constraint 2.18 $\alpha + \beta = 1$ and replacing α by $1 - \beta$ give:

$$x_i(1 - \beta) + y_i\beta = z_i \quad (2.20)$$

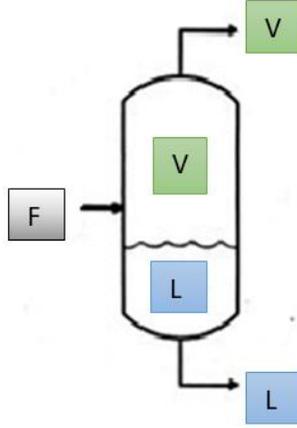


Figure 6 Two phase system

now by introducing equilibrium ratio Eq. (2. 15) into Eq. (2. 20)

$$y_i\beta + \frac{y_i}{K_i}(1 - \beta) = z_i \quad (2.21)$$

now solving for y_i

$$y_i = \frac{z_i K_i}{1 + \beta(K_i - 1)} \quad (2.22)$$

Applying constraint (2.18)

$$\sum_{i=1}^c \frac{z_i K_i}{1 + \beta(K_i - 1)} = 1 \quad (2.23)$$

This equation is important for us; we call it an *objective function* because we can use it as the starting point for solving the vapor-liquid equilibrium problems we have posed. However, as you may be thinking right now, this is not the only choice that we have for an *objective function*. In fact, we may obtain another *objective function* if we repeat the previous steps, while solving instead for x_i and having

$$\sum_{i=1}^c \frac{z_i}{1 + \beta(K_i - 1)} = 1 \quad (2.24)$$

Both (2. 23) and (2. 24) are plausible *objective functions*. Either of them allows us to solve the

flash problem that we are dealing with. The variables that make up both equations are:

C = Number of components

z_i = Overall composition (Feed composition)

K_i = Equilibrium ratios of each of the components of the mixture

β = Vapor fraction in the system.

What is it that we are looking for? Go back and look at the types of VLE problems that we would like to solve, as we presented them in the previous section. If we are interested in solving the *flash problem*, we want to know how much liquid and gas we will have inside the flash equilibrium cell. This is, given a liquid-vapor mixture of composition z_i and C number of components, what percent of the total number of moles is liquid, and what percent is vapor? How do we split it? In this case, we would like to come up with a value for α and β respectively.

Both Eq.s (2. 23) and (2. 24) give us the answer for these questions taking into consideration that we do have “Known K_i ”, but keep in mind that K_i are functions of the pressure, temperature, and composition of the system.

For the time being, let us assume that we do have valuable K_i 's. Two questions remain unanswered:

1. First, is it “better” to solve the problem using Eq. (2. 23) or (2. 24)?
2. Second, how do we solve for β ? For a complex mixture of many components, “ β ” cannot be calculated explicitly.

We will address both of these questions in the next sections.

2.4.1.8 Analysis of the Objective Functions and the Need for Rachford-Rice Equation

In a previous module we derived two different objective functions (Eq. 2. 23 & 2.2 4) for the purpose of solving the flash equilibrium problem. These equations arise from simple mole balances and the concept of equilibrium ratios. In addition, we have assumed that K_i 's are obtained where the only unknown will be β or molar fraction of one phase while the molar fraction for the other phase is calculated from complimentary equation that state all molar fraction sum up to unity.

Once we are able to solve for molar fraction of the phase, by implementing Eq. 2. 22 or similar equation for x_i . In other words, phase compositions of the present phases at equilibrium can be solved. However, one question that raised up in section before that how we can solve for molar fraction where we can notice that both equations are nonlinear in molar phase fraction. This mean that we cannot solve the molar phase fraction explicitly as function of other variable where iterative techniques are required such as *Newton-Raphson* approach. A distinctive characteristic of any *Newton-Raphson* procedure is that the success of the procedure depends greatly upon the choice of the initial guess for the variable considered. In fact, it is very commonly said that for *Newton-Raphson* to converge, the initial guess must be as close as possible to the real solution. This ‘ill-

nesses become worse when dealing with non-monotonic functions. In a monotonic function, derivatives at every point are always of the same sign where the function either increases or decreases monotonically. For *Newton-Raphson*, this means that there are neither valleys nor peaks that could lead the procedure to false solutions. If we apply *Newton-Raphson* to a monotonic and everywhere-continuous function, the success of the procedure is *not* strongly dependent on the initial guess. In fact, if we apply *Newton-Raphson* to a monotonic function that is continuous at every single point of the domain as well, it does not matter at all where you start: you will always find *the* solution. It might take time to achieve convergence, but you will be able to converge to a unique solution.

Based on these facts and that neither Eq. 2. 23 nor 2. 24 are not monotonic which make the convergence to be harder to be achieved and having a correct solution. (Rachford (1952)) Solved this problem by defining a new monotonic objective function so to simplify the iteration procedure using both Eq. 2. 23 & 2.24 but in a different form respectively as following where α_g molar phase fraction of vapor is phase

$$F_y(\alpha_g) = \sum_{i=1}^c \frac{z_i K_i}{1 + \alpha_g (K_i - 1)} - 1 = 0 \quad (2.25)$$

$$F_x(\alpha_g) = \sum_{i=1}^n \frac{z_i}{1 + \alpha_g (K_i - 1)} - 1 = 0 \quad (2.26)$$

where the combination yield

$$F_s = F_y(\alpha_g) - F_x(\alpha_g) \quad (2.27)$$

$$F(\alpha_g) = \sum_{i=1}^n \frac{z_i (K_i - 1)}{1 + \alpha_g (K_i - 1)} = 0 \quad (2.28)$$

Eq.(2.28) is the Rachford-Rice Equation. In order to demonstrate the monotonic behavior of this equation, the first derivative of Rachford-Rice show that the outcome of this summation will be always positive due to the square's presence both in numerator and denominator and that overall composition z_i is always positive

$$F'(\alpha_g) = \sum_{i=1}^n \frac{z_i (K_i - 1)^2}{\{1 + \alpha_g (K_i - 1)\}^2} = 0 \quad (2.29)$$

We have already answered to the questions that have raised up in the last section where one question remains unanswered:

In the previous development, we made one crucial assumption. We assumed that, somehow, we knew all the equilibrium ratios. The fact is, however, that we usually don't. If we do not know all

equilibrium ratios, then all of the previous discussions are meaningless. So far, the only conclusion we can draw is that if that we should find a way to know K_i 's so that the VLE problem is *solvable*. by doing that we conclude the discussion about VL equilibria (Two phase equilibria).

2.4.1.9 Obtaining K_i 's Equilibrium Ratios

The K_i value of each component in a real hydrocarbon mixture is a function of the pressure, temperature and also of the composition of each of the phases. Since the compositions of the phases are not known beforehand, equilibrium constants are not known, either. If they were known, the VLE calculation would be performed in a straightforward manner.

Nevertheless, the good news is that *sometimes* K_i 's are fairly independent of the phase's composition. This is true at pressure and temperature conditions away from the critical point of the mixture. Therefore, numerous correlations have been developed throughout the years to estimate the values of K_i for each hydrocarbon component as a function of the pressure and temperature of the system. The values produced from this correlation are called Ideal K_i 's and can be used for first estimation in the iteration procedure after that and based on the results obtained, they can be updated using different iterative procedure such as *Successive substitution* (SS) or *accelerated successive substitution* (aSS) in some cases especially near to the critical point and sometimes Newton-Raphson.

A very popular empirical correlation that is very often used in the petroleum and natural gas industry is *Wilson's empirical correlation* for initializing the algorithm or as initial guess is as following (M. Michelsen (1982a))

$$K_i = \frac{P_{ci}}{P} \exp \left[5.373(\omega_i) \left(1 - \frac{T_{ci}}{T} \right) \right] \quad (2.30)$$

T_{ci} is critical temperature, in °R or K, P_{ci} , critical pressure, in psi, kPa or bar, ω_i is the acentric factor, P is the system pressure, in psi, kPa or bar, T is the system temperature, in °R or K. (P and P_c , T and T_c must be in the same units.) This correlation can be considered accurate at low and moderate pressure, up to about 3.5 MPa (500 psia) where the K-values are assumed to be independent of composition “ideal K_i 's”.

2.4.1.10 Summary

In previous sections we have discussed that all system at equilibrium regardless of how many phases they will be present can be solved and formulated using the Three step application procedure. In fact, any engineering problem can be solved in the same way. We start by describing the system that we want to solve by finding an equation that describe the system of interest and may help to formulate the problem mathematically. In our case (phase equilibria problem) classical thermodynamic provide the mathematical language to formulate and solve the problem. For this purpose, we described the problem as function of chemical potential and free energy where we reduced this condition so to be valuable for engineering purposes. This step has been achieved

using some auxiliary function such as fugacity and fugacity coefficient in this case (VLE) while in other cases like hydrate the need of activity coefficient is necessary in some cases. However, the procedure that should be followed so to solve the problem must have a physical meaning to what is actually present in the system in the real world. Based on that we defined K_i 's ratios where it has been merged with mass balance calculations later on. The result of which two non-monotonic objective function can be used to solve the problem.

Due to the nature of the phase equilibria problem and available data it has been concluded that iterative technique is necessary such as Newton-Raphson. After careful analysis of the objective functions and iterative procedure chosen so that to obtain a valuable and correct result the need of a monotonic objective function appeared. Thanks to (Rachford (1952)) and solution provided for this problem a new objective function has been found. Finally, we concluded that obtaining a mathematical solution for phase equilibria problem can be achieved under the circumstances that equilibrium ratio can be obtained. Where K_i 's are value of each component in a real hydrocarbon mixture is a function of the pressure, temperature and also of the composition of each of the phases which are not known in advance we concluded that the well-known correlation in oil and gas industry Wilson's empirical correlation can be used as a first estimate for initiating the algorithm. However, we should keep in mind that all of this discussion and the procedure followed is made under the assumption that the system will split, and two-phase system will be formed. This obstacle will be discussed in the followed sections of this chapter. At the end phase equilibria problem is summarized and presented in the algorithm below taking into consideration that relationship for fugacity and fugacity coefficient with T , P and phase composition are present in our hand (will be discussed later).

2.4.1.11 Algorithm

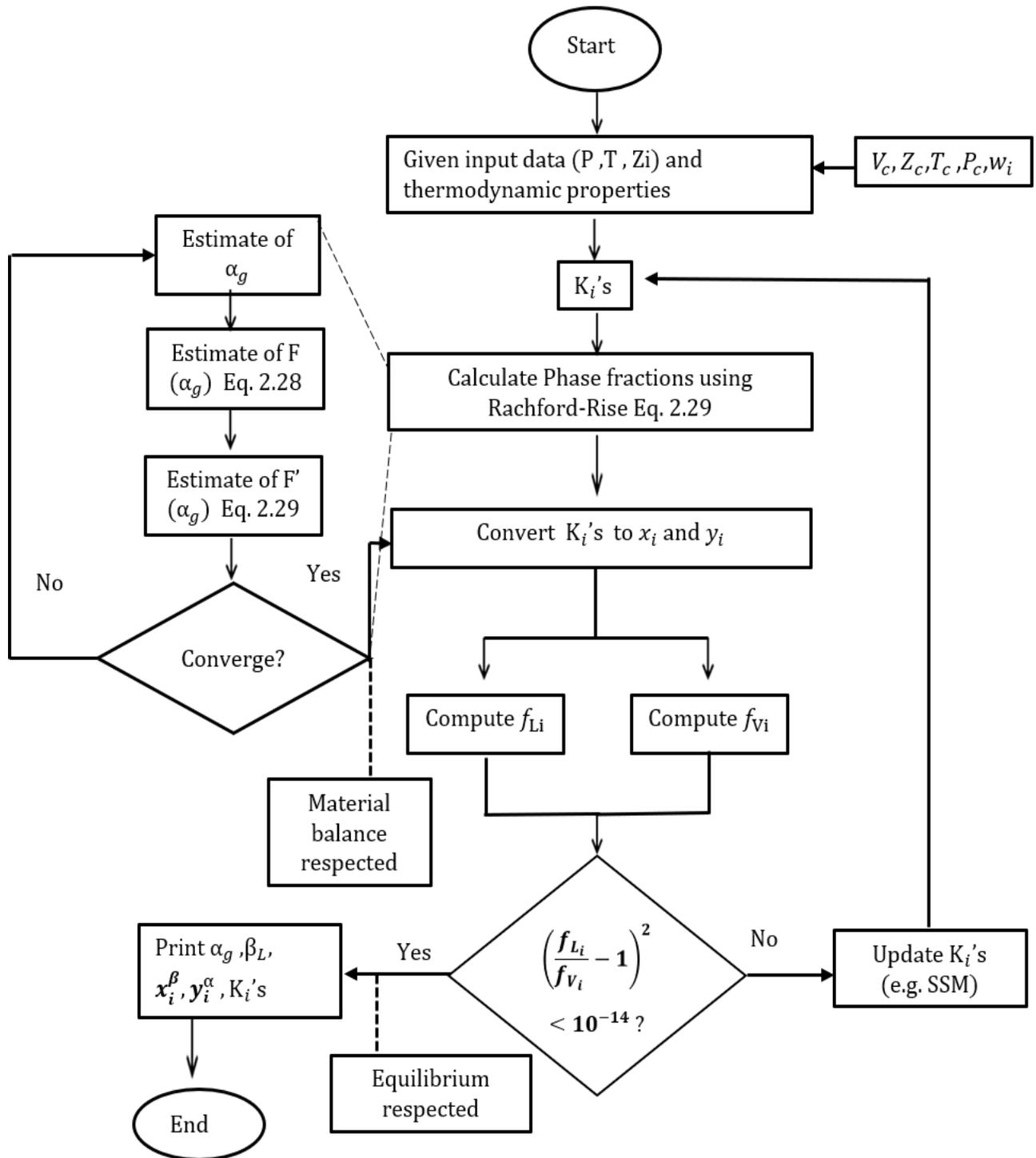


Figure 7 Typical Algorithm for Two phase flash system (produced in this work).

2.5 Multiphase Equilibria

Multiphase flash equilibria are important in petroleum engineering for which water and hydrocarbons mixtures, hydrocarbon and CO₂ rich mixtures and hydrocarbon methane rich mixtures can encounter in reservoir performance and recovery studies. In this area mostly VLLE is encountered as multiphase flash while in hydrate and flow assurance, VLLE, SLVE, SSVE and many others can be present. Moreover, one of the most difficult aspects of making VLLE or VLE calculations may not be the calculation itself but knowing whether or not a hydrocarbon mixture will actually be present as two or three phases at equilibrium for a pressure and temperature condition. When things come to hydrates it became more difficult due to the fact that seven phases may be present such as: ice, aqueous water, vapor, liquid hydrocarbons, hydrate type I, II and H without mentioning the fact of presence of salts or TH inhibitors in the system or the transition of fluids phases and hydrate consequently. In this case the solution or algorithm consists of finding the correct number and types of phases and their corresponding equilibrium compositions such that the Gibbs free energy of the system is at the global minimum.

Based on that in this section we are expanding the theory of VLE explained before so that to be applicable for multiphase flash or hydrate equilibrium. In addition, (Gupta 1990) phase stability approach that is applied already in CSMGem solution will be discussed and imbedded in the algorithm.

2.5.1 Thermodynamic Equilibrium Constraint and Equilibrium Ratios

As it has been showed in section 5.1.4. That the constraint for chemical equilibrium can be imposed in terms of fugacity, the same constraint is implied in multiphase flash calculation. It is not more or less fundamental than chemical potential equality constraints but easier to understand and to be correlated to pressure, temperature and composition of different phases present at equilibrium. As a result, the fugacity of all component in all phases of the system must be equal so to respect the following condition:

$$\frac{f_{ir}}{f_{ik}} = \frac{x_{ir}\phi_{ir}p}{x_{ik}\phi_{ik}p} = 1 \quad (2.31)$$

$$i = 1, \dots, C \quad k = 1, \dots, \pi$$

Where f_{ik} and f_{ir} are the fugacity of component i in phase k and reference phase r present at equilibrium, respectively. However, equilibrium ratio can be also defined from Eq. (2.31) as the ratio of fugacity coefficients of component i between phase k and the reference phase, r so to be written as:

$$k_{ik} = \frac{\phi_{ir}}{\phi_{ik}} = \frac{x_{ik}}{x_{ir}} \quad (2.32)$$

$$i = 1, \dots, C \quad k = 1, \dots, \pi \quad (2.33)$$

Note that if the phases at equilibrium are known a priori, this approach is valid also. For VLE phase equilibria described in the section before the reference phase was defined indirectly as liquid hydrocarbon where the k phase represented is the vapor one. However, hydrate problem dictates that the phases are not known a priori so that a generalized form must be derived such that it is valid for all phases (present or not) so that to be able to proceed with the necessary calculation required for each system (e.g VLE, SLLE...). Thanks to (Gupta 1990) and (M. Michelsen (1982a)) that they provided phase stability analysis for this brick wall.

2.5.2 Gupta's Approach

The main objective of (Gupta 1990) was to find a way so that to detect if a phase will be present at equilibrium or not. He analyzed thermodynamic equilibrium constraint using Eq. (2. 31) and stated the following

$$\frac{f_{ir}}{f_{ik}} \begin{cases} = 1 & \text{if phase } k \text{ present at equilibrium} \\ < 1 & \text{if phase } k \text{ not present at equilibrium} \end{cases}$$

$$i = 1, \dots, C \quad k = 1, \dots, \pi$$

Keeping in mind that a reference phase is always present and defined in advance, Eq. (2.32) show that for any phase k ($k \neq r$) that is present at equilibrium, the fugacity of each component in that phase must be equal to that in the reference phase. Conversely, for any phase that is not present, the fugacity of each component in that phase is larger than that in the reference phase (the tendency of component escaping is higher and not equal so the phase cannot be present at equilibrium).

(Gupta 1990) Took advantage of both cases and multiplied the equilibrium ratio in Eq. (2. 32) by the fugacity ratio in Eq. 2. 33, so to have:

$$k_{ik} = \frac{\Phi_{ir}}{\Phi_{ik}} = \frac{x_{ik} f_{ir}}{x_{ir} f_{ik}} \quad i = 1, \dots, C \quad k = 1, \dots, \pi \quad (2.34)$$

After that he introduced the natural log to the quotient of fugacity Eq. (2. 35) where θ_k is defined as stability variable as following

$$k_{ik} = \frac{x_{ik}}{x_{ir}} \exp \left[-\ln \frac{f_{ik}}{f_{ir}} \right] \quad (2.35)$$

$$\theta_k = \ln \frac{f_{ik}}{f_{ir}} \quad (2.36)$$

thus

$$k_{ik} = \frac{x_{ik}}{x_{ir}} \exp[-\theta_k] \quad (2.37)$$

rewriting Eq. 2. 37 in terms of the mole fraction ratio as

Eq. 2.38 can be applied for all phases regardless of the phase's presence in the system at equilibrium. (Gupta 1990) Showed that defining the mole fraction ratio in this manner is equivalent to

$$\frac{x_{ik}}{x_{ir}} = k_{ik} e^{\theta_k} \quad i = 1, \dots, C \quad k = 1, \dots, \pi \quad (2.38)$$

minimizing the Gibbs energy of the system conditional to

$$S_k = \alpha_k \theta_k = 0 \quad k = 1, \dots, \pi \quad (2.39)$$

that is, if

- $\alpha_k > 0$ then phase k is present and $\theta_k = 0$
- $\alpha_k = 0$ then phase k is not present and $\theta_k \neq 0$

2.5.3 Mass Balance (Rachford-Rice Extension and Gupta's Parameter Implementation)

In section 5.1.7 we have shown how to derive mole fraction and two objective function from simple mole balances and equilibrium ratios. In this way these equations can be expanded in the same basis matter so to be valid for multiphase systems. However, in this section we are showing the extended equations for multiphase flash calculation including Gupta's parameters for stability analysis purpose. Note that in VLE section we have defined indirectly that the reference phase is liquid hydrocarbon one while in multiphase flash the following expression for the composition of component i in the reference phase including Gupta stability parameter is as following:

$$x_{ir} = \frac{z_i}{1 + \sum_{\substack{k=1 \\ k \neq r}}^{\pi} \alpha_k (k_{ik} e^{\theta_k} - 1)} \quad i = 1, \dots, C \quad (2.40)$$

Using equation 2.38 and recognizing that $k_{ir} = 1$ and $\theta_k=0$, Equation 2.40 can be rewritten for component i in any phase k as

$$x_{ik} = \frac{z_i K_{ik} e^{\theta_k}}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} \quad (2.41)$$

$$i = 1, \dots, C \quad k = 1, \dots, \pi$$

By implementing constraint 2. 18b that state the summarization of all components in phase k must be equal to unity, we get the objective function, I_k , for each phase

$$I_k = \sum_{i=1}^C \frac{z_i K_{ik} e^{\theta_k}}{1 + \sum_{\substack{j=1 \\ j \neq 1}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} - 1 = 0 \quad (2.42)$$

$$k = 1, \dots, \pi (k \neq r)$$

By further substituting constraint 2. 18b for the reference phase into Eq. 2. 42, we get extended Rachford-Rice equation for multiphase flash including phase stability Gupta's parameter as

Which must be satisfied for all phases (present or not) at a solution. In order to have only the extended Rachford-Rice equation for Multiphase system ignore the exponent both in nominator and denominator in the equation above

2.5.4 Solving For Thermodynamic Equilibrium

Traditionally, there are a total of $(I+C) \cdot \pi - I$ unknowns in solving for thermodynamic equilibrium.

$$I_k = \sum_{i=1}^C \frac{z_i (K_{ik} e^{\theta_k} - 1)}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} = 0 \quad (2.43)$$

$$k = 1, \dots, \pi$$

For a closed system of C components and π possible phases at a given temperature and pressure. For example, for a VLE equilibrium system of five components the number of unknowns is six which are four mole composition and one phase fraction we solve for while others can be obtained from complimentary equations (e.g. constraints 2. 18a and 2. 18b). In this case while introducing an extra set of unknowns (the stability variables), the unknowns present are in the order of $(2+C) \cdot \pi - 2$ as following:

$$x_{ik} \quad i = 1, \dots, C \quad k = 1, \dots, \pi \quad \{\pi \cdot C \text{ unknowns}\}$$

$$\alpha_k \quad k = 1, \dots, \pi \quad (k \neq r) \quad \{\pi - 1 \text{ unknowns}\}$$

$$\theta_k \quad k = 1, \dots, \pi \quad (k \neq r) \quad \{\pi - 1 \text{ unknowns}\}$$

The number of unknowns to solve while using the above approach is certainly of the same order of magnitude and so does not require much more computation. In fact, the difference in the number of unknowns is only $\pi - 1$. However, the solution procedure is split into two parts:

1. Minimizing Gibbs energy by updating phase amounts and stability variables at a given set of K values and
2. Updating K -values at a given set of phase amounts and stability variables. This approach is typical in phase equilibria problems such as this.

2.5.4.1 Minimizing Gibbs Energy (At A Given Phase Fractions/Compositions)

Different iterative procedure can be used so to minimize the Gibbs energy of the system at a given set of K-values. The one that is mostly implied for such problems is Newton-Raphson. Using extended Rachford-Rice equation for multiphase with Gupta's constraint, convergency can be achieved as long as fugacity coefficients are not strong functions of composition. This is certainly the case for the fluid phases such as vapor and liquid hydrocarbon in VLE near to or at the critical point but is not necessarily true for the aqueous and hydrate phases in our case here.

In order to implement or to use the Newton procedure, the derivatives of Equation 2. 43 are needed with respect to each unknown variable α_j and θ_j . In addition, the simple derivatives of Equation 2. 39.

The derivatives of Eq. 2. 43 with respect to each variable are as following:

$$\frac{\partial I_k}{\partial \alpha_j} = - \sum_{i=1}^c \frac{z_i (K_{ik} e^{\theta_k} - 1) (K_{ij} e^{\theta_j} - 1)}{\left(1 + \sum_{\substack{m=1 \\ m \neq r}}^{\pi} \alpha_m (K_{im} e^{\theta_m} - 1)\right)^2} \quad \begin{matrix} k = 1, \dots, \pi (k \neq r) \\ j = 1, \dots, \pi (j \neq r) \end{matrix} \quad (2.44)$$

$$\text{and} \quad \frac{\partial I_k}{\partial \theta_j} = - \sum_{i=1}^c \frac{z_i (K_{ik} e^{\theta_k} - 1) \alpha_j K_{ij} e^{\theta_j}}{\left(1 + \sum_{\substack{m=1 \\ m \neq r}}^{\pi} \alpha_m (K_{im} e^{\theta_m} - 1)\right)^2} \quad \begin{matrix} k = 1, \dots, \pi (k \neq r) \\ j = 1, \dots, \pi (j \neq r) \end{matrix} \quad (2.45)$$

However, we have just mentioned in this work Multiphase flash equilibria problem but taking into consideration solving for temperature or pressure as it is the case in VLE other problem mentioned in the specific section in which a given phase forms having molar fraction phase in the magnitude of \mathcal{E} , the following derivative of Equation 2. 43 is given:

$$\frac{\partial I_k}{\partial P} = \frac{\partial I_k}{\partial T} = \sum_{i=1}^c x_{ir} \left[\frac{\partial K_{ik}}{\partial P \text{ or } \partial T} e^{\theta_m} - \frac{(K_{ik} e^{\theta_k} - 1) \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j \frac{\partial K_{ij}}{\partial P \text{ or } \partial T} e^{\theta_j}}{\left(1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)\right)} \right] \quad (2.46)$$

However, the derivative of the K-values with respect to T or P is still needed. It is assumed, for this derivative, that the K-values are constant in composition and change only with temperature and pressure. Due to the complexity of the equations of state used, numerical approximation can be used (e.g. forward). Going back to main task Multiphase flash and stability the Newton method gives a correction to the phase amounts and stability variables based on the gradient of the Gibbs energy at the given set of K-values. Due to the highly non-ideal behavior of the hydrate phases, some restriction may be needed so to avoid an ad rapt change set in the variables that we are iterating for.

2.5.4.2 Updating K-Values and Composition at A Given Gibbs Energy

After that Gibbs energy is minimized at a given set of K-values, the K's need to be updated together with composition. Equation 2. 41 is used to update the composition of each phase. With the new composition, the fugacity coefficients are calculated to get the new set of K-values. Successive substitution or accelerated successive substitution iteration of the composition can be used to achieve convergence. However, due to the highly non-ideal behavior of the hydrate phases, equation mentioned before can be replaced with fractional occupancy of guest molecule in hydrate cavities (will be explained after) to update the composition.

2.5.5 Ki's Values for Hydrate Problem

In order to initialize Gibbs energy minimization algorithm explained in the last sections, Ki series values for $(\pi-1)$ number of phases need to be defined. In the same case of VLE where ideal K values (composition independent) set can defined for vapor/liquid hydrocarbon using Wilson empirical correlation as first estimate, in hydrate also we are seeking expressions and empirical correlations for distribution of components between each phase with respect to the reference phase that is always present at equilibrium. This expressions or approaches should be at least sufficient as a starting value in the algorithm. Before doing so, let's have a look on hydrate phase diagram so to have clear understanding of what phases can be present first.

Based on P-T hydrate diagram, the phases that can be present at equilibrium are ice, liquid water, liquid hydrocarbon, vapor and hydrate. Note that hydrates can form different structures (I, II and H) as well where several researchers have developed expressions for distribution of guest molecules between the vapor and hydrate phase, some of them produced K-values independent on hydrate structure while some others (S.L.Mann 1989) developed K-values structure dependent. However, the most common set of K-values implemented these days and the different software used in this work (e.g. CSMGem, HydraFLASH) are structure dependents ones. Additionally, to that in case of salts and thermodynamic inhibitors presence in the system additional set of Ki's are required (e.g. Salts in the aqueous phases).

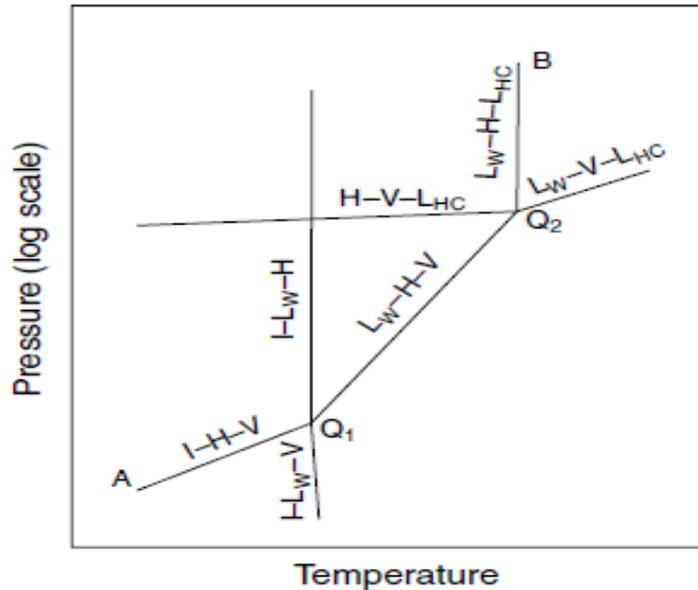


Figure 7 Illustrative phase diagram for gas hydrates. Lines correspond to three-phase equilibrium, separating the two-phase regions. The label corresponds to liquid water (Lw), ice (I), hydrate (H), vapor (V) and liquid hydrocarbons (LHC). The intersection of the three-phase lines corresponds to the quadruple point (Q1) and (Q2), where I-Lw-H-V and Lw-H-V-LHC coexist respectively (Sloan ED 2008)

2.5.6 Definition of the Reference Phase

Figure 7 and 2.2.5 section show that different possible phases can be present at equilibrium in hydrate (e.g. Ice or Liquid water). However, in order to define the necessary K-value series, a reference phase that will present at equilibrium should be known a priori Eq. (2. 42).

In VL equilibria we have defined indirectly and in advance that in case that the system will split at certain temperature and pressure liquid hydrocarbon will be present and adopted as the reference one. In hydrate that is not the case while we don't know in advance if ice or liquid water, vapor or liquid hydrocarbon will be present. In order to solve this issue and have a physical solution during the iterative process, several reference may be tested by implying some hints like if temperature is less 273.15 K the algorithm will start assuming ice and if it is higher liquid water can be assumed and tested. Note that all phases may be a reference phase except for the hydrate phases while the order of preference can differentiate from one to other.

2.5.7 Algorithm

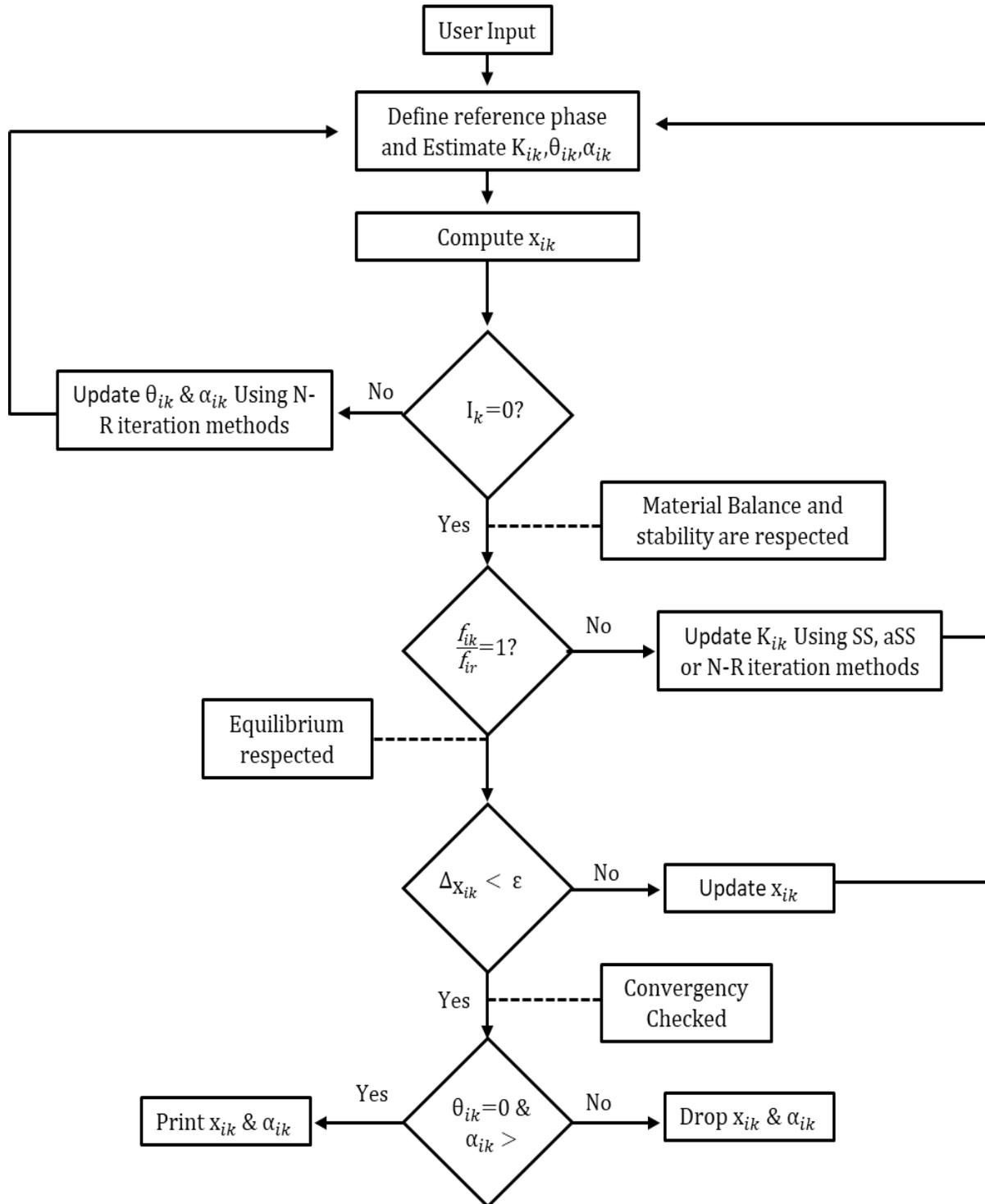


Figure 8 Algorithm for multiphase flash problems including Gupta's stability analysis (produced in this work).

Chapter 3

3 Cubic Plus Association Eos

In Chapter 2 we have explained the concept of a flash equilibria problem for Two (VLE) and Multiphase flash systems. In addition, we have described the chemical equilibrium using fugacity and fugacity coefficient as auxiliary functions instead of abstract chemical equilibrium while we didn't mention how these parameters can be calculated or correlated with the intensive properties of our interest. However, values of this function can be obtained in several way (e.g. Charts, Correlations etc.). One of these ways is using an EoS. Referring to that, for petroleum and reservoir engineers most important EoSs are the cubic ones (e.g. SRK, PR) which perform very well for simple gases and hydrocarbon mixtures. These equations fail to produce satisfactory results for more complex fluids such as polar solvents, electrolytes, heavy petroleum residual fluids like asphaltenes, polymers, and surface-active agents wherein either more sophisticated molecular interactions or more complicated molecular structure and characteristics contribute to the microscopic and macroscopic fluid properties encountered in hydrate such as water, inhibitors, alcohols. However, the key to model macroscopic properties of a fluid is the ability to describe microscopic properties so to account for intermolecular and intermolecular interactions of the real complex fluids. Based on that, hydrates calculations show the need for an equation of state that cover all obstacles mentioned before so to ensure a achieving a correct solution of the problem. Thanks to (Georgios M. Kontogeorgis 2006) who provided such equation known as CPA EoS which stands for Cubic Plus Association equation of state. This equation is a combination of SRK or PR equations of state and association term of the SAFT/Wertheim theory. Therefore, the equation of CPA EoS has two parts, the non-association term and association term. The development of CPA started in 1995 as a research project funded by Shell (Amsterdam) and the model was first published in 1996. Since then, it has been successfully applied to a variety of complex phase equilibria including mixtures containing alcohols, glycols, water and hydrocarbon.

In this chapter we will describe the CPA EoS that started gaining more attention in the last decade in flow assurance field. Nowadays it represents the most accurate model in thermodynamic modelling of hydrates. CPA EoS is used in four approaches tested in this work implemented in two well-known software for predicting hydrate dissociation pressure and temperature in the today's market such as Hydra Flash (Hydra Fact company/Heriot-Watt University) and Multiphase Flash (KBC/Schlumberger). In order to have a full understood of the equation and how it functions SAFT model also will be discussed briefly.

3.1 Introduction

(Chapman W.G. (1990)) Proposed an equation of state by applying the Wertheim thermodynamic perturbation theory referred as SAFT, an acronym for Statistical Association Fluid Theory. In the original SAFT approach, molecules are considered as single (spherical particles) or multiple chained hard-sphere segments (non-spherical molecules) with or without association sites depending on whether the molecule can form hydrogen bonding or not. Therefore, SAFT EoS is expressed

as the sum of non-association contributions which account for non-polar interactions, e.g. intermolecular interaction between non-polar compounds like hydrocarbon and gases and association contribution which accounts for hydrogen bonding between polar components such as water, alcohols etc.

A research team in University of Denmark then took advantage of the capabilities of PR and SRK equations of state in modelling the phase equilibria of non-polar systems and combine them with the association term of the SAFT EoS to also cover the hydrogen bonding of polar fluids. Species forming hydrogen bonds often exhibit unusual thermodynamic behavior. The strong attractive interactions between molecules of the same species (self-association) or between molecules of different species (cross-association). These interactions may strongly affect the thermodynamic properties of the fluids. Thus, the chemical equilibria between clusters should be taken into account in order to develop a reliable thermodynamic model.

The Cubic-Plus-Association (CPA) model is an equation of state that combines the cubic equation of state and an association (chemical) term described below. In terms of the compressibility factor Z it has an appearance:

$$Z = Z^{SRK} + Z^{assoc} \quad (3.1)$$

the compressibility factor contribution from the SRK equation of state is:

$$Z^{SRK} = \frac{V_m}{V_m - b} - \frac{a(T)}{RT(V_m + b)} \quad (3.2)$$

and the contribution from the association term is given by:

$$Z^{assoc} = \sum_i x_i \sum_i \rho_i \sum_{A_i} \left[\left(\frac{1}{X_{A_i}} - \frac{1}{2} \right) \frac{\partial X_{A_i}}{\partial \rho_i} \right] \quad (3.3)$$

where V_m is the molar volume, X_{A_i} is the mole fraction of the molecule i not bonded at site A . i.e. the monomer fraction and x_i is the superficial (apparent) mole fraction of component i . The small letter i is used to index the molecules and capital letters A are used to index the bonding sites on a given molecule.

While the SRK model accounts for the physical interaction contribution between the species, the association term in CPA takes into account the specific site-site interaction due to hydrogen bonding. The association term employed in CPA is identical with the one used in SAFT.

Before describing the model, a brief definitions and explanation of “sites” and “site-related” parameters used in CPA and SAFT models is given below.

3.2 Association Energy and Volume Parameters

The key features of the hydrogen-bonds are their strength, short range and high degree of localization. In Fig. 13 it is shown a simple example of prototype spheres, or spherical segments, with one associating site, A. Such spheres can only form an AA-bonded dimer when both distance and orientation are favorable.

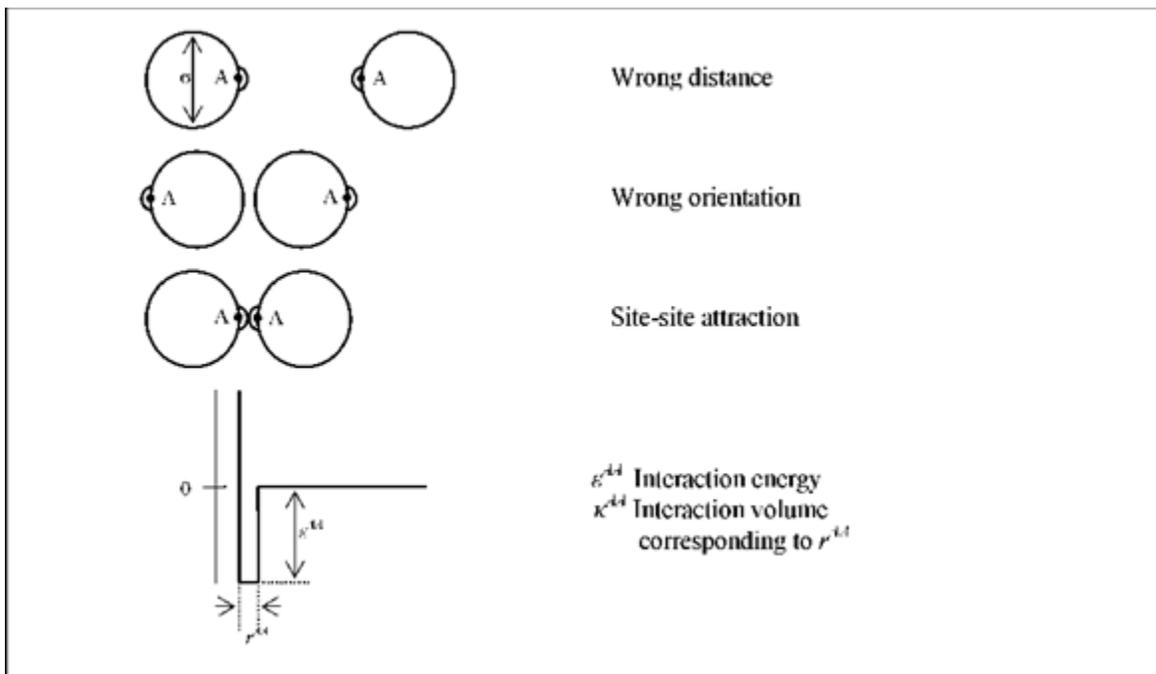


Figure 9 Model of hard spheres with a single associating site A illustrating a simple case of molecular association due to short-distance, highly orientational, site-site attraction (Chapman W.G. (1990)).

The associating bond strength is quantified by a square-well potential, which, in turn, is characterized by two parameters. The parameter ϵ^{AA} characterizes the association energy (well depth) and the parameter k^{AA} characterizes the association volume (corresponds to the well width r^{AA}). In general, the number of association sites on a single molecule is not constrained and they are labelled with capital letters A, B, C, etc. Each association site is assumed to have a different interaction with the various sites on another molecule. Examples of two associating sites molecules are given in the Fig. 10.

Thus, for each pure component three molecular parameters, σ , ϵ/k and m are needed, which are the temperature independent segment diameter in angstroms, the Lennard-Jones interaction energy in Kelvins, and the number of segments per chain molecule, respectively. In addition, two association parameters, association energy, ϵ^{AA}/k in Kelvins and volume k^{AA} (dimensionless), for each site-site interaction. The usual method for deriving the σ , ϵ and m values is to fit vapor pressure and density data for pure components. The association parameters ϵ^{AiBj}/k and k^{AiBj} can be fitted to bulk phase equilibrium data.

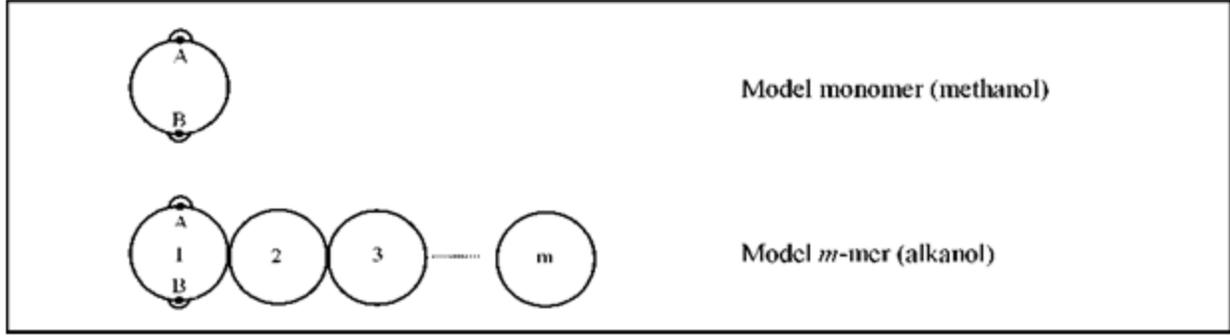


Figure 10 Models of hard sphere (monomer) and chain (m-mer.) molecules with two associating sites A and B; the chain molecule represents non- spherical molecule (Chapman W.G. (1990)).

3.3 Association Term in CPA Eos

For pure components, the association term is defined in terms of the residual Helmholtz energy a^r per mole, defined as

$$a^r(T, V, n) = a(T, V, n) - a^{ig}(T, V, n) \quad (3.4)$$

Where a and a^{ig} are the total Helmholtz energy per mole and the ideal gas Helmholtz energy per mole at the same temperature and density. The residual Helmholtz energy is a sum of three terms representing contributions from different intermolecular forces: segment-segment interaction, covalent chain-forming bonds and site-site specific interactions among the segments, for example, hydrogen-bonding interactions:

$$a^r = a^{seg} + a^{chain} + a^{assoc} \quad (3.5)$$

The extension of the CPA EoS to mixtures requires mixing rules only for the parameters of the SRK-part, while the extension of the association term to mixtures is straightforward. The mixing and combining rules for a and b are the classical van der Waals one.

The mixture Helmholtz energy for the association term is linear with respect to mole fractions,

n_i :

$$\frac{A^{assoc}}{RT} = \sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \quad (3.6)$$

Here, A is used to index bonding sites on a given molecule and X_{A_i} denotes the fraction of A - sites on molecule i that do not form bonds with other active sites and Σ represents a sum over all associating sites. Examples for molecules with two attractive sites and one attractive site are given as follows (Chapman W.G. (1990))

$$\frac{A^{assoc}}{RT} = \ln X^A - \frac{X_A}{2} + \ln X^B - \frac{X_B}{2} + 1 \quad (2 \text{ sites}) \quad (3.7)$$

$$\frac{A^{assoc}}{RT} = \ln X^A - \frac{X_A}{2} + \frac{1}{2} \quad (1 \text{ sites}) \quad (3.8)$$

3.3.1 Fraction of Non-Bonded Associating Molecules, X_A

Since the mixture contains not only monomer species but also associated clusters, we need to define the mole fraction for the total components and their monomers. The mole fraction of all the molecules of component i is X_i . The mole fraction of (chain) molecules i that are NOT bonded at site A is X_{A_i} and hence $1-X_{A_i}$ is the mole fraction of molecules i that are bonded at site A. This definition applies to both pure self-associated compounds and to mixture components and is give in terms of mole numbers.

The site fractions in Eq. (4. 6), X_{A_i} is related to the association strength between site A on molecule i and site B on molecule j , Δ^{AiBj} and the fractions X_{B_i} of all other kind of association sites B by:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{AiB_j}} \quad (3.9)$$

where ρ is the molar density of the fluid and n_j mole fraction of substance j .

However, the key quantity in CPA and SAFT EoS is the association strength Δ . In SAFT it is approximated by the following equation

$$\Delta^{AB} = g(d)^{seg} \left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1 \right] (\sigma^3 \kappa^{AB}) \quad (3.10)$$

$$g(d)^{seg} \approx g(d)^{hs} = \frac{2 - \eta}{2(1 - \eta)^3} \quad (3.11)$$

Since CPA is a molecular based (not a segment based) EoS, (Kontogeorgis G.M. 1996) proposed to calculate the reduced fluid density by

$$\eta = \frac{b}{4V} \quad (3.12)$$

where $b = 2\pi N_{AV} d^3 / 3$ and substituted the product $\sigma^3 \kappa^{AB}$ in Eq. (4. 10) by equivalent $b\beta$.

So, in CPA, Δ^{AiBi} , the association (binding) strength between site A on molecule i and site B on molecular j is given by:

$$\Delta^{A_i B_j} = g(\rho)^{ref} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (3.13)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume of interaction between site A of molecule i and site B of molecule j , respectively and $g(\rho)^{ref}$ is the radial distribution function for the reference fluid.

The hard-sphere radial distribution is further simplified by (Kontogeorgis G.M. 1996) to:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \& \quad \eta = \frac{1}{4} b\rho \quad (3.14)$$

also (Yakoumis I.V. (1997)) proposed a much simpler general expression for the association term instead of Eq. (4. 3):

$$Z^{assoc} = -\frac{1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i n_i \sum_{A_i} (1 - X_{A_i}) \quad (3.15)$$

where

$$\frac{\partial \ln g}{\partial \rho} = \frac{\partial \ln \left(\frac{1}{1 - 1.9\eta} \right)}{\partial \rho} = \frac{1.9(b/4)}{1 - 1.9\eta} \quad (3.16)$$

$$\rho \frac{\partial \ln g}{\partial \rho} = \frac{1.9\eta}{1 - 1.9\eta} \quad (3.17)$$

In term of Volume, we have the results of sCPA and CPA, respectively:

$$\rho \frac{\partial \ln g}{\partial \rho} = \frac{0.475B}{V - 0.475B} \quad (3.18)$$

$$\rho \frac{\partial \ln g}{\partial \rho} = 2B \frac{(10V - B)}{(8V - B)(4V - B)} \quad (3.19)$$

The resulting EoS is referred to as simplified CPA (sCPA). Phase equilibria calculations performed in this work are based on the original CPA model.

3.3.2 Association Schemes

As seen from Eq. (4. 15), the contribution of the association compressibility factor in CPA depends on the choice of association scheme, i.e. number and type of association sites for the associating compound.

(Huang S.H. (1990)) Have classified eight different association schemes, which can be applied to

different molecules depending on the number and type of associating sites. Examples of one-, two-, three- and four-site molecules for real associating fluids are given in Fig. 14. According to them, for example, for alkanols, each hydroxylic group (OH) has three association sites, labelled A, B on oxygen and C on hydrogen. The association strength Δ due to the like, oxygen-oxygen or hydrogen-hydrogen (AA, AB, BB, CC) interactions is assumed to be equal to zero (since two lone pairs electrons on protons cannot attract each other). The attraction can only occur between a lone pair electron and proton, i.e. the only non-zero Δ is due to the unlike (AC and BC) interactions, which moreover are considered to be equivalent. Another approximation is to allow only one site of oxygen (A) and one site of hydrogen (B). In case of self-association, the association scheme for alkanols is 2B.



Figure 11 Types of bonding in real associating fluids (Huang S.H. (1990))

The 2B association scheme (Huang S.H. (1990))

$$\Delta^{AA} = \Delta^{BB} = 0 \quad (3.20)$$

$$\Delta^{AB} \neq 0$$

$$X_A = X_B = \frac{-1 + \sqrt{1 + 4\rho\Delta^{AB}}}{2\rho\Delta^{AB}} \quad (3.21)$$

The 4C association scheme (Huang S.H. (1990))

$$\Delta^{AA} = \Delta^{AB} = \Delta^{BB} = \Delta^{CC} = \Delta^{CD} = \Delta^{DD} = 0 \quad (3.22)$$

$$\Delta^{AC} = \Delta^{AD} = \Delta^{BC} = \Delta^{BD} \neq 0$$

$$X_B = X_C = X_D = \frac{-1 + \sqrt{1 + 8\rho\Delta^{AC}}}{4\rho\Delta^{AC}} \quad (3.23)$$

These schemes are in agreement with the accepted physical picture that alcohols form linear oligomers and water three-dimensional structures.

When CPA is used for the cross-associating mixture, e.g. alcohols-water, combining rules are needed for the cross-association energy and volume parameters (ϵ_{AiBj} , β_{AiBj}) or for the association strength Δ^{AiBj} . Examples for the selection of the combining rule are given by (Fu Y-H. (1995)). According to them, in water-alcohol mixture, water has three association sites and an

alcohol has two, but only the unbounded electron pair can form a hydrogen bond with a hydrogen atom thereafter Eq. (3. 22) can be described to all sites in methanol-water system:

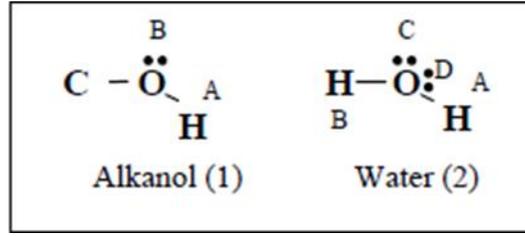


Figure 12 association sites for alkanol and water

The scheme of self-association: A1B1, A2C2, B2C2 and the scheme of cross association A1C2, A2B1, B2B1 (Kraska 1998) then we rewrite Eq. (3. 9) as

$$X_{A_1} = \frac{1}{1 + \rho(n_1 X_{B_1} \Delta^{A_1 B_1} + n_2 X_{C_2} \Delta^{A_1 C_2})} \quad (3.24)$$

$$X_{B_1} = \frac{1}{1 + \rho(n_1 X_{A_1} \Delta^{A_1 B_1} + n_2 X_{B_2} \Delta^{B_1 B_2} + n_2 X_{A_2} \Delta^{B_1 A_2})} \quad (3.25)$$

$$X_{C_2} = \frac{1}{1 + \rho(n_2 X_{A_2} \Delta^{C_2 A_2} + n_2 X_{B_2} \Delta^{C_2 B_2} + n_1 X_{A_1} \Delta^{C_2 A_1})} \quad (3.26)$$

$$X_{B_2} = \frac{1}{1 + \rho(n_2 X_{C_2} \Delta^{B_2 C_2} + n_1 X_{B_1} \Delta^{B_2 B_1})} \quad (3.27)$$

$$X_{A_2} = \frac{1}{1 + \rho(n_2 X_{C_2} \Delta^{A_2 C_2} + n_1 X_{B_1} \Delta^{A_2 B_1})} \quad (3.28)$$

If we set $\Delta^{A_2 C_2} = \Delta^{B_2 C_2}$, $X_{A_2} = X_{B_2}$ we have:

$$X_{A_1} = \frac{1}{1 + \rho(n_1 X_{B_1} \Delta^{A_1 B_1} + n_2 X_{C_2} \Delta^{A_1 C_2})} \quad (3.29)$$

$$X_{B_1} = \frac{1}{1 + \rho(n_1 X_{A_1} \Delta^{A_1 B_1} + 2n_2 X_{B_2} \Delta^{B_1 A_2})} \quad (3.30)$$

$$X_{C_2} = \frac{1}{1 + \rho(2n_2 X_{A_2} \Delta^{C_2 A_2} + n_1 X_{A_1} \Delta^{C_2 A_1})} \quad (3.31)$$

$$X_{A_2} = X_{B_2} = \frac{1}{1 + \rho(n_2 X_{C_2} \Delta^{B_2 C_2} + n_1 X_{B_1} \Delta^{B_2 B_1})} \quad (3.32)$$

There are four non-linear equations with four variables and we can solve them simultaneously using Newton-Raphson method with objective function (for all sites):

In order to simplify the problem further, all the cross-association energy and volume parameters

$$F \left(\sum_{X_{A_i}}^{all\ sites} X_{A_i} \right) = X_{A_1} \left(1 + \rho \sum_j n_j \sum_{B_i} X_{B_j} \right) - 1 \approx 0 \quad (3.33)$$

are taken to be equal and are estimated as follows:

$$\varepsilon^{A_1 B_2} = \varepsilon^{B_1 B_2} = \varepsilon^{C_1 A_2} = \sqrt{\varepsilon^{A_1 C_1} \varepsilon^{A_2 B_2}} \quad (3.34)$$

$$\beta^{A_1 B_2} = \beta^{B_1 B_2} = \beta^{C_1 A_2} = \frac{(\beta^{A_1 C_1} + \beta^{A_2 B_2})}{2} \quad (3.35)$$

According to (Derawi S.O. 2002) following mixing rules for the energy parameters shows good Correlation with the experimental data on methanol-water system:

$$\text{CR-1:} \quad \varepsilon^{A_i B_j} = \frac{\varepsilon^{A_1 B_1} + \varepsilon^{A_2 B_2}}{2} \quad ; \quad \beta^{A_i B_j} = \sqrt{\beta^{A_1 B_1} + \beta^{A_2 B_2}} \quad (3.36)$$

$$\text{CR-2:} \quad \varepsilon^{A_i B_j} = \sqrt{\varepsilon^{A_1 B_1} + \varepsilon^{A_2 B_2}} \quad ; \quad \beta^{A_i B_j} = \sqrt{\beta^{A_1 B_1} + \beta^{A_2 B_2}} \quad (3.37)$$

$$\text{Elliot Rule:} \quad \Delta^{A_i B_j} = \sqrt{\Delta^{A_1 B_1} + \Delta^{A_2 B_2}} \quad (3.38)$$

Chapter 4

4 Hydrates Thermodynamic Modelling

Predicting hydrate stability/formation conditions is crucial for oil and gas industry mainly to avoid pipelines blockage during oil and gas transportation and supplying. Additionally, exploitation methods of the natural gas in hydrate started gaining attention in the last years for which understanding under what conditions hydrates are stable or can be stabilized is also important. Based on that, in this Chapter we will begin with a quick review of relatively simple hand calculations, while the main objective is to discuss original and modified van der Waals-Platteeuw (vdW-P) theory and finishing with implementation of this theory in different computer-based calculations using different rigorous thermodynamic models present in different software used in this study.

4.1 Introduction and Review of First Hydrate Prediction Methods

Hydrate hand prediction methods for hydrate stability were largely developed between 1940s and 1950s and based mainly on experimental work. These relatively simple and eloquent methods, before the days of computers, were powerful in allowing one to predict hydrate stability for the first time, often quite accurately (Wilcox WI 1941). However, sH hydrate structure had not yet been discovered at this time, these early hand calculation models can be applied only to the sI and sII hydrates. Most popular and widely used hand calculations methods are the gas gravity and the k-value methods. The “Gas Gravity Method” is the simplest method for predicting hydrate formation at three-phase hydrate-liquid water-vapor equilibrium. This method was presented by Katz in 1945 and it is based solely on one data information the density of a natural gas. Plotted on a P-T diagram. As the work of Katz mainly considered hydrates formed from natural gasses, the gas gravity method should be used only for systems of natural gasses with low contents of non-combustible compounds (such as e.g. carbon dioxide, nitrogen etc.) (Sloan ED 2008). Another method was developed a few years earlier, called the “distribution coefficient method” or in short, the “K-value method”. The K-value method assumes ideal solution of gas phase constituents in the solid hydrate phase. Under this assumption, a distribution coefficient of each hydrate former is defined as

$$K_{v-s,i} = \frac{y_i}{Y_i} \quad (4.1)$$

Where y_i is the vapor phase mole fraction of component i and Y_i is the water-free hydrate mole fraction of component i . Water-free means that the mole fraction is calculated only on basis of the hydrate phase guest contents. Again, charts were produced, presenting K-values as function of temperature and pressure for individual hydrate formers.

Using of these charts and the following constraint

$$\sum_{i=1}^n \frac{y_i}{K_{v-s,i}} \quad (4.2)$$

Hydrate formation conditions could be estimated by an iterative solution approach.

K-value method provides accurate temperature/pressure dissociation conditions for light gases found in typical natural gases. On the other hand, this method shown deviation from experimental data for

- Mixtures with high ethane, propane and butane contents.
- Two gases of main interest in this work, carbon dioxide and nitrogen (Sloan ED 2008).

4.2 Original Van Der Waals-Platteeuw Hydrate Model

The van der Waals-Platteeuw hydrate theory was proposed by J. H. van der Waals and J. C. Platteeuw in 1958 (J.H.van der Waals 1959). vdW-P treats the solid phase only and is combined with an equation of state and an activity coefficient model for the description of co-existing fluid phases. Nowadays the typical equation of state used in this model is CPA EoS explained in chapter 3 since it covers all type of fluids. The basic theory behind the model presented by van der Waals and Platteeuw is often claimed to come from statistical mechanics. (Sloan ED 2008) Have shown a detailed derivation of the model equations by the use of statistical mechanics. However, the model can similarly be derived by use of chemical reaction theory and classical thermodynamic relations.

The main assumption in the Van der Waals-Platteeuw theory is the chemical potential of water in the hydrate phase. As it has been shown in Chapter 2 that at equilibrium, the chemical potential must be equal in all phases present at. As an example of hydrate case and in the locus of hydrate (H) – Ice (I) – vapor (V) equilibrium, the following expression must be satisfied:

$$\mu_{water}^{Hydrate} = \mu_{water}^{Ice} = \mu_{water}^{Vapor} \quad (4.3)$$

The idea of vdW-P followed the same Three-Step procedure mentioned in Chapter 2 where they spliced the problem into three Steps. In Step 1 they assumed that water will form empty cage with the same structure conditions (e.g. same volume) as actual hydrates but without the presence of guest molecule inside. Step 2 evaluate the chemical potential of water in this theoretical empty hydrate and after that imply the physics in step 3 so that the problem will be physically valuable. Step 3 implies the adsorption of gas guest molecules into the empty hydrate cage. By doing that they solved the hydrate problem indirectly but implementing the main engineering paths so to have a solution of the real difficult problem. This meta-stable hydrate crystalline water β -phase that constituted the same structure of water as in the actual hydrate, cannot be present or formed experimentally. This is present due to the fact that hydrate is formed and stabilized given that pressure inside of crystalline hydrate cages is equal to pressure outside so no burst or collapse of hydrate cages may happen. This stabilization is present by the interaction between the guest molecule (gas)

and its surrounding water molecules forming the cage. In the following sections of this chapter we will describe vdW-P theory for the second locus of P-T diagram hydrate forming (Hydrate (H) – Liquid water (Lw) – vapor (V)).

The difference in chemical potential of actual hydrate phase and meta-stable β -phase can be described as following:

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H \quad (4.4)$$

For Step 3 in which the adsorption of guest molecules in empty cavities has been taken into consideration an adsorption theory is required. This step can be described by an approach similar to Langmuir adsorption theory using Lennard-Jones-Devonshire theory for the description of the Langmuir adsorption coefficients. (Prausnitz W. 1972).

In order to do so, several assumptions have to be taken into consideration (Prausnitz W. 1972) such as:

- 1) All cavities are assumed spherical.
- 2) Each cavity can contain one guest at most.
- 3) Guest-Guest interactions are negligible.
- 4) The guest molecule does not distort the structural properties of the water lattice.
- 5) The internal partition function of the guest is considered to be identical to that of the gas in its ideal state.
- 6) Only London forces are considered in the guest-host interaction.

The main reason for these assumptions goes back to monolayer adsorption theory of Langmuir that will be used while additional assumptions will be discussed later in the appropriate sections.

As it is mentioned before that the difference in chemical potential of water between the theoretical empty hydrate water lattice (empty cavities) and the actual hydrate is the presence of guest molecules in the water cavities, according to monolayer Langmuir adsorption theory this difference can be illustrated in Fig.13 and described as following:

$$\Delta\mu(T, P, \theta)_w^{\beta-H} = -R.T. \sum_m \left[v_m \cdot \ln \left(1 - \sum_j \theta(T, P, \bar{y})_{m,j} \right) \right] \quad (4.5)$$

where

- v_m is the number of cavities type m per water molecule in the hydrate structure.
- $\theta(T, P, \bar{y})_{m,j}$ is the fractional occupancy of component j in cavity type m
- R is the universal, or ideal gas constant.

- T is the absolute temperature of the system.

and $\theta(T, P, \bar{y})_{m,j}$ can be described by

$$\theta(T, P, \bar{y})_{m,j} = \frac{C(T)_{m,j} \cdot f(T, P, \bar{y})_j}{1 + \sum_l C(T)_{m,l} \cdot f(T, P, \bar{y})_l} \quad (4.6)$$

where

- $f(T, P, \bar{y})_j$ is the fugacity of hydrate former (gas guests) in the vapor phase.
- $C(T)_{m,j}$ is the Langmuir constant for gas component j in cavity type m .

additionally, $f(T, P, \bar{y})_j$ can be expressed in terms of fugacity coefficient and partial pressure

$$f(T, P, \bar{y})_j = \varphi(T, P, \bar{y})_j \cdot y_j \cdot P \quad (4.7)$$

for which

- $\varphi(T, P, \bar{y})_j$ is fugacity coefficient of hydrate former in vapor phase.
- y_j is the mole fraction of component j in vapor phase.

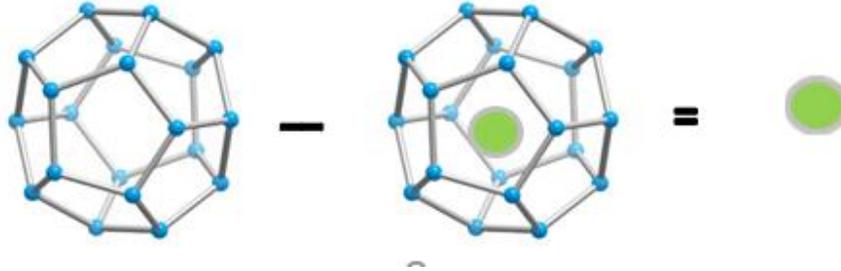


Figure 13 Illustration of Equation (4. 5) stating vdW-P concerning difference of metastable and actual hydrate phase (picture belong to this work)

Substitution of Equation (4. 6) into Equation (4. 5) obtains the following expression for the difference of chemical potential of water between hypothetical and actual hydrate

$$\Delta\mu(T, P, \theta)_w^{\beta-H} = R \cdot T \cdot \sum_m \left[v_m \cdot \ln \left(1 + \sum_j C(T)_{m,j} \cdot f(T, P, \bar{y})_j \right) \right] \quad (4.8)$$

Whereas we have considered that hydrate is formed in the second locus (Hydrate (H) – Liquid water (Lw) – vapor (V)) at equilibrium the following equation is true

$$\mu_{water}^{Hydrate} = \mu_{water}^{Liquid\ water} \quad (4.9)$$

in which chemical potential of water is as following

$$\mu_{water}^{Liquid\ water} = \mu(T, P)_w^p + R. T. \ln[\gamma(T, P, \bar{x})_w^{Lw}] \quad (4.10)$$

where

- $\mu(T, P)_w^p$ is the chemical potential of pure liquid water
- γ is the activity coefficient of water in the non-ideal liquid phase at the presence of hydrogen bonding or electrolyte components in the liquid phase (e.g. MEG, Salts).

However, several studies have shown that solubility of hydrocarbons gasses is very low in which the activity coefficient can be assumed unity (close to ideal). However, in case of carbon dioxide and nitrogen the solubility is countable where the activity coefficient is calculated properly. On the other hand, activity coefficient is important in hydrate case in the presence of salts and alcohols.

Activity coefficient can be modeled either with symmetric activity coefficient model γ or in terms of fugacity coefficients ϕ as following

$$\gamma(T, P, \bar{x})_w^{Lw} = x_w^{Lw} \cdot \gamma(T, P, \bar{x})_w^{Lw} = x_w^{Lw} \cdot \frac{\phi(T, P, \bar{x})_w^{Lw}}{\phi(T, P)_w^p} \quad (4.11)$$

where x_w^{Lw} is the liquid phase composition in water.

Defining the difference of chemical potential between the theoretical clathrate and a pure water liquid phase thusly

$$\Delta\mu(T, P)_w^{\beta-Lw} = \mu(T, P)_w^\beta - \mu(T, P)_w^{pLw} \quad (4.12)$$

Substituting Eq. (4. 4), (4. 9), (4. 10), (4. 11) and (4. 12) hence $\Delta\mu(T, P)_w^{\beta-Lw}$ can be formulated as

$$\begin{aligned} \Delta\mu(T, P)_w^{\beta-Lw} = R. T. \sum_m \left[v_m \cdot \ln \left(1 + \sum_j C(T)_{m,j} \cdot f(T, P, \bar{y})_j \right) \right] \\ + R. T. \ln \left[x_w^{Lw} \cdot \frac{\phi(T, P, \bar{x})_w^{Lw}}{\phi(T, P)_w^p} \right] \end{aligned} \quad (4.13)$$

or

$$\begin{aligned} \Delta\mu(T, P)_w^{\beta-Lw} = R. T. \sum_m \left[v_m \cdot \ln \left(1 + \sum_j C(T)_{m,j} \cdot f(T, P, \bar{y})_j \right) \right] \\ + R. T. \ln \left[x_w^{Lw} \cdot \gamma(T, P, \bar{x})_w^{Lw} \right] \end{aligned} \quad (4.14)$$

Keep in mind that all fugacity and fugacity coefficients in Eq. (4. 14) can be calculated using CPA EoS explained in Chapter 3. Alternatively, some approaches tested in this work use activity coefficient model where Eq. (4. 14) is used.

4.2.1 Langmuir Adsorption Coefficient $C(T)_{m,j}$

(J.H.van der Waals 1959) Suggested that the Langmuir adsorption coefficients may be approximated using Lennard-Jones-Devonshire cell theory for example Lennard-Jones 12-6 cell potential. They suggested the usage of the following expression

$$C(T)_{m,j} = \frac{4 \cdot \pi}{(k_B \cdot T)} \cdot \int_0^\infty \exp \left[\frac{-w(r)_{m,j}}{(k_B \cdot T)} \right] \cdot r^2 \cdot dr \quad (4.15)$$

for which

- k_B is Boltzmann constant.
- $w(r)_{m,j}$ is the spherical core cell potential of component j in cavity type m .
- r is the linear distance from the center of the cell.

Several researchers investigated different cell potentials for use in hydrate dissociation pressure calculations. The most suitable for this kind of calculation is Kihara cell potential (McKoy 1963). They work where based on evaluating the interactions between the guest molecule and all its surrounding first layer of water molecules forming cages and summed up the contributions in one expression for the spherical core cell potential. In the years after, (Prausnitz W. 1972) were the first who presented an algorithm for vdW-P for hydrate model for computer calculation and slightly modified the expression provided by (McKoy 1963) to became:

$$w(r)_{m,j} = 2 \cdot z_m \cdot \varepsilon_j \cdot \left[\frac{\sigma_j^{12}}{R_m^{11} \cdot r} \cdot \left(\delta(N = 10)_{m,j} + \frac{a_j}{R_m} \cdot \delta(N = 11)_{m,j} \right) - \frac{\sigma_j^6}{R_m^5 \cdot r} \cdot \left(\delta(N = 4)_{m,j} + \frac{a_j}{R_m} \cdot \delta(N = 5)_{m,j} \right) \right] \quad (4.15)$$

where

- z_m is the coordination number for the guest in cavity type m .
- ε_j is the characteristic energy of guest molecule j .
- a_j is the core radius of molecule j .
- $\sigma_j + 2a_j$ is the collision diameter of molecule j .
- R_m is the radius of cavity type m .

And $\delta(N)_{m,j}$ is reported as

$$\delta(N)_{m,j} = \frac{1}{N} \cdot \left[(1 - r \cdot R_m^{-1} - a_j \cdot R_m^{-1})^{-N} - (1 + r \cdot R_m^{-1} - a_j \cdot R_m^{-1})^{-N} \right] \quad (4.17)$$

Different methods have been investigated to solve the integral of Langmuir constant in Eq. (4. 15) such as Simpson 3/8 rule and the Gauss-Legendre Quadrature method.

4.3 Parrish and Prausnitz Hydrate Modelling

Parrish and Prausnitz (Prausnitz W. 1972) hydrate modeling carried out in CSMHyd Software (Colorado School of Mineral)

4.3.1 Model Theory

(Prausnitz W. 1972) Have implemented vdW-P theory of hydrate to be in a state suitable for computer calculation. P-P presented hydrate-gas equilibria calculation for multicomponent gas systems based on the usage of Kihara (spherical-core). The ideas of these researches are as following.

With theoretical chemical potential derived by (J.H.van der Waals 1959) showed in the last section, (Prausnitz W. 1972) proposed a method for calculating the chemical potential difference by the use of experimental reference hydrate. This method took advantage on the fact that chemical potential is a state function and by integrating the value of experimental reference hydrate, chemical potential of hydrate at desired pressure and temperature can be calculated. They defined a reference hydrate at reference temperature, T_o , and reference pressure, P_o , where the integration to the desired state is done following two steps. First step aims to transform the measured chemical potential difference from reference temperature T_o , to the actual temperature T and from reference P_o at reference temperature T_o , to the reference pressure P_R at the actual temperature, T . In the second step, the chemical potential difference is transformed from the reference pressure P_R to the actual pressure P . two steps are as following:

Step 1:

$$\begin{aligned} \frac{\Delta\mu(T, P_R)_w^{\beta-L_w}}{R \cdot T} &= \frac{\Delta\mu(T_o, P_o)_w^{\beta-L_w}}{R \cdot T_o} - \int_{T_o}^T \frac{\Delta H(T_o, P_o)_w^{\beta/Ice} + \Delta H(T)_w^{Ice/L_w}}{R \cdot T^2} dT \\ &+ \int_{T_o}^T \frac{\Delta V_w^{\beta/Ice} + \Delta V(T)_w^{Ice/L_w}}{R \cdot T} \cdot \frac{dP_R}{dT} dT \end{aligned} \quad (4.18)$$

where

- $\Delta\mu(T, P_R)_w^{\beta-L_w}$ is the chemical potential difference between theoretical empty hydrate and liquid water at temperature T and at the dissociation pressure of the reference pressure P_R .
- $\Delta\mu(T_o, P_o)_w^{\beta-L_w}$ is the chemical potential difference between theoretical empty hydrate and liquid water at temperature T_o and at the dissociation pressure of the reference pressure P_o .

- $\Delta H(T_0, P_0)_{w}^{\beta/ice}$ is the molar enthalpy difference between empty hydrate and ice.
- $\Delta H(T)_{w}^{ice/Lw}$ is the molar enthalpy difference between ice and liquid water.
- $\Delta V_{w}^{\beta/ice}$ is the difference in molar volume of the empty hydrate and ice measured for the reference hydrate.
- $\Delta V(T)_{w}^{ice/Lw}$ is the difference in molar volume of ice and liquid water.
- $\frac{dP_R}{dT}$ is the slope of the measured dissociation pressure-temperature curve reported by (Prausnitz W. 1972) for the reference hydrate.

Parrish and Prausnitz didn't reported how they obtained this function. In addition, no place this derivative is present. However, in this work we have derived this function for better understanding and explanations of results.

$$\begin{aligned} \frac{\Delta\mu_w^{\beta-Lw}}{RT} &= \frac{\mu_w^{\beta} - \mu_w^{Lw}}{RT} = \frac{\mu_w^{\beta}}{RT} - \frac{\mu_w^{Lw}}{RT} = \frac{\mu_{w_0}^{\beta}}{RT_0} - \frac{\mu_{w_0}^{Lw}}{RT_0} + \frac{\mu_w^{\beta}}{RT} - \frac{\mu_w^{Lw}}{RT} \\ &= \frac{\Delta\mu_{w_0}}{RT_0} + \frac{\Delta\mu_w^{\beta-Lw}}{RT} \end{aligned} \quad (4.19)$$

For pure species $\Delta\mu_w = \Delta G_w$ (4.20) and $\Delta G_w = V\Delta P - S\Delta T$ (4.21) where

$$S = \frac{\Delta H}{T} \quad (4.22)$$

$$\frac{\Delta\mu_w^{\beta-Lw}}{RT} = \frac{\Delta\mu_{w_0}^{\beta-Lw}}{RT_0} + \frac{V^{\beta-Lw} dP}{RT} - \frac{(\Delta H)^{\beta-Lw} dT}{RT^2} \quad (4.23)$$

Splicing each parameter into phase intervals (Ice – Liquid water)

$$\begin{aligned} \frac{\Delta\mu_w^{\beta-Lw}}{RT} &= \frac{\Delta\mu_{w_0}^{\beta-Lw}}{RT_0} + \left[\frac{V^{\beta-ice}}{RT} dP + \frac{V^{ice/Lw}}{RT} dP \right] \\ &\quad - \left[\frac{\Delta H^{\beta-ice}}{RT^2} dT + \frac{\Delta H^{ice/Lw}}{RT^2} dT \right] \end{aligned} \quad (4.24)$$

Rearranging and integrating Eq. (4.24)

$$\begin{aligned} \frac{\Delta\mu_w^{\beta-Lw}}{RT} &= \frac{\Delta\mu_{w_0}^{\beta-Lw}}{RT_0} \\ &\quad + \left[\int_{P_0}^P \frac{V^{\beta-ice} + V^{ice/Lw}}{RT} dP - \int_{T_0}^T \frac{\Delta H^{\beta-ice} + \Delta H^{ice/Lw}}{RT^2} dT \right] \end{aligned} \quad (4.25)$$

Replacing dP by slope of pressure-temperature reference diagram provided by Parrish and Prausnitz $\frac{dP_R}{dT}$ in Eq. (4. 25) so to have the general form present in Eq. (4. 18)

It should be noted that $\Delta H(T)_w^{Ice/Lw}$ is function of two terms, the first one is the change of enthalpy due to the phase change from ice to liquid at the reference temperature and the second term is the heat capacity of liquid water contribution of the heating from the reference temperature to the actual temperature. These two terms are covered in the following equation:

$$\Delta H(T)_w^{Ice/Lw} = \Delta H(T_0, P_0)_w^{Ice/Lw} + \Delta C_p(T) \cdot (T - T_0) \quad (4.26)$$

Parrish and Prausnitz presented the reference pressure P_0 as the vapor pressure of ice at temperature T_0 and since this pressure is too small with respect to hydrate dissociation pressure it is assumed 0.

Step 2:

$$\begin{aligned} \Delta\mu(T, P)_w^{\beta-Lw} &= \Delta\mu(T, P_R)_w^{\beta-Lw} \\ &+ \left(\Delta V_w^{\beta/Ice} + \Delta V(T)_w^{Ice/Lw} \right) \cdot (P - P_R) \end{aligned} \quad (4.27)$$

where

- $\Delta\mu(T, P)_w^{\beta-Lw}$ Is the actual chemical potential difference between theoretical empty hydrate and liquid water at temperature T and at the dissociation pressure of the actual pressure P .
- $\Delta\mu(T, P_R)_w^{\beta-Lw}$ Is the chemical potential difference between theoretical empty hydrate and liquid water at temperature T and at the dissociation pressure of the reference pressure P_R calculated in Step 1.

Parrish and Prausnitz (Prausnitz W. 1972) provided a three parameters expression for the temperature dependence of the reference hydrate dissociation pressure:

$$\ln[P_R/atm] = A_R + \frac{B_R}{T} + C_R \cdot \ln T \quad (4.28)$$

And as it is obvious that dissociation pressure is gas composition dependence that may form structure sI and sII, (Prausnitz W. 1972) used as a reference hydrate for sI for temperature below 0°C xenon and methane hydrate for temperature above this temperature. For sII bromochlorodifluoromethane hydrate has been considered as reference hydrate for temperature below 0°C and natural gas mixture hydrate data above it. The values are shown in the following Table 1.

Table 2 Constants reported by (Prausnitz W. 1972) for reference hydrate dissociation pressure calculation

Parameters	sI Hydrate	sII Hydrate
$\Delta \mu(T_0, P_0)_{water}^{Liq/Water} / (J \cdot mol^{-1})$	1264	882.8
$\Delta H_{water}^{\beta/Ice} / (J \cdot mol^{-1})$	1151	807.5
$\Delta H(T_0)_{water}^{\beta/Ice \rightarrow liquid} / (J \cdot mol^{-1})$	-6009	-6009
$\Delta C_P(T) / J \cdot K^{-1} \cdot mol^{-1}$	38.11-0.1406. (T-273.1)	38.11-0.1406. (T-273.1)
$(\Delta V_{water}^{\beta/Ice}) \cdot 10^6 / (m^3 \cdot mol^{-1})$	3.0	3.4

Parameters	$P_R/atm, T/K > 273$	$P_R/atm, T/K > 273$
A_R	-1212.2	-1023.14
B_R	44344.0	34984.3
C_R	187.719	159.923
	$P_R/atm, T/K < 273$	$P_R/atm, T/K < 273$
A_R	23.0439	11.5115
B_R	-3357.57	4092.37
C_R	-1.85000	0.316033

In addition, P-P proposed an expression for calculation of the Langmuir adsorption coefficients and noted that this expression is favorable in the temperature range (260-300) K. they recommended the usage of this expression for simplicity in the temperature range while for temperature outside of it, Kihara cell potential (Eq. 4. 16) should be used with parameters of Table 2. However, they stated that the proposed equation for Langmuir adsorption coefficients deviation is 0.2% or less for each gas in the temperature range. The proposed expression given as

$$C_{mj}(T) = \left(\frac{A_{mj}}{T}\right) \exp\left(\frac{B_{mj}}{T}\right) \quad (4.29)$$

where

- A_{mj} And B_{mj} are fitting parameters related to guest type j in cavity type m present in Table 3. In case of occupancy of a guest in both structure sI for example methane where sI hydrate structure include two cavity type four fitting parameter is required for this guest.

Table 3 Kihara Parameters reported by (Prausnitz W. 1972) used in CSMHyd

Gas	$2a_j, \text{\AA}$	$\sigma, \text{\AA}$	$\epsilon/k \text{ }^\circ\text{K}$
Methane	0.600	3.2398	153.17
Ethane	0.800	3.3180	174.97
Ethylene	0.940	3.2910	172.87
Propane	1.360	3.3030	200.94
Propylene	1.300	3.2304	202.42
Cyclopropane	1.000	3.4559	210.58
Isobutene	1.600	3.1244	220.52
Nitrogen	0.700	3.6142	127.95
Oxygen	0.720	2.7673	166.37
Carbone dioxide	0.720	2.9681	169.09
Hydrogen sulfide	0.720	3.1558	205.84
Argon	0.368	2.9434	170.50
Krypton	0.460	2.9739	198.34
Xenon	0.560	3.1906	201.34
Sulfur hexafluoride	1.620	3.1379	220.73

During describing hydrate modeling three step procedure that Van-der-Waals -Platteeuw have used to describe and solve the problem, many assumptions has been made regarding the solution of Step 3 (adsorption phenomenon). However, one major assumption is that guest molecule does not distort the structural properties of the water lattice. This assumption means that the Gibbs energy change is only due to adsorption of guest molecule with no volume change of the cages when gas is adsorbed in. Parrish and Prausnitz took advantage of this assumption and equalized the theoretical chemical potential difference of each state to its equivalent experimental one so to be able to solve the problem directly for dissociation pressure or temperature.

Note that all equations derived above can be implied only for second locus of P-T hydrate equilibrium (above ice-point). For equilibrium calculation below ice point (first locus) Eq. (4. 14) will be

$$\Delta\mu(T, P)_w^{\beta-Ice_w} = R.T. \sum_m \left[v_m \cdot \ln \left(1 + \sum_j C(T)_{m,j} \cdot f(T, P, \bar{y})_j \right) \right] \quad (4.29)$$

and Eq. (4. 18)

$$\begin{aligned} \frac{\Delta\mu(T, P_R)_w^{\beta-Ice_w}}{R.T} &= \frac{\Delta\mu(T_0, P_0)_w^{\beta-Ice_w}}{R.T_0} - \int_{T_0}^T \frac{\Delta H(T_0, P_0)_w^{\beta/Ice}}{R.T^2} dT \\ &+ \int_{T_0}^T \frac{\Delta V_w^{\beta/Ice}}{R.T} \cdot \frac{dP_R}{dT} dT \end{aligned} \quad (4.30)$$

and new parameter is required for Eq. (4. 19) while Eq. (4. 20) will be

$$\Delta\mu(T, P)_w^{\beta-Ice_w} = \Delta\mu(T, P_R)_w^{\beta-Ice_w} + \left(\Delta V_w^{\beta/Ice} \right) \cdot (P - P_R) \quad (4.31)$$

Now in CSMHyd Software Parish and Prausnitz has been implemented with a modification of Two-step calculation which has been replaced by (Holder 1988) equation. This equation eliminated the need for the reference pressure and thus simplified the calculations given us:

$$\begin{aligned} \frac{\Delta\mu(T, P)_w^{L_w}}{R.T} &= \frac{\Delta\mu(T_0, P_0)_w^{L_w}}{R.T_0} - \int_{T_0}^T \frac{\Delta H(T_0, P_0)_w^{\beta/Ice} + \Delta H(T)_w^{Ice/L_w}}{R.T^2} dT \\ &+ \int_0^P \frac{\Delta V_w^{\beta/Ice} + \Delta V(T)_w^{Ice/L_w}}{R.T} \cdot dP \end{aligned} \quad (4.32)$$

Table 4 Parameters for calculating Langmuir constant for structure sI & sII (Prausnitz W. 1972)

Gas	Small, °K		Large, °K	
	$A_{ml} \times 10^3$	$B_{ml} \times 10^{-3}$	$A_{ml} \times 10^2$	$B_{ml} \times 10^{-3}$
Methane	3.7237	2.7088	1.8372	2.7379
Ethane	0.0	0.0	0.6906	3.6316
Ethylene	0.0830	2.3969	0.5448	3.6638
Cyclopropane	0.0	0.0	0.1449	4.5796
Nitrogen	3.8087	2.2055	1.8420	2.3013
Oxygen	17.3629	2.2893	5.7732	1.9354
Carbone dioxide	1.1978	2.8605	0.8507	3.2779
Hydrogen sul- fide	3.0343	3.7360	1.6740	3.6109
Argon	25.7791	2.2270	7.5413	1.9181
Krypton	16.8620	2.8405	5.7202	2.4460
Xenon	4.0824	3.6063	2.0657	3.4133
Structure II cavities				
Methane	2.9560	2.6951	7.6068	2.2027
Ethane	0.0	0.0	4.0818	3.0384
Ethylene	0.0641	2.0425	3.4940	3.1071
Propane	0.0	0.0	1.2353	4.4061
Propylene	0.0	0.0	2.0174	4.0057
Cyclopropane	0.0	0.0	1.3136	4.6534
Isobutene	0.0	0.0	1.5730	4.4530
Nitrogen	3.0284	2.1750	7.5149	1.8606
Oxygen	14.4306	2.3826	15.3820	1.5187
Carbone dioxide	0.9091	2.6954	4.8262	2.5718
Hydrogen sul- fide	2.3758	3.7506	7.3631	2.8541
Argon	21.8923	2.3151	186.6043	1.5387

4.3.2 Algorithm for Hydrate Dissociation Pressure

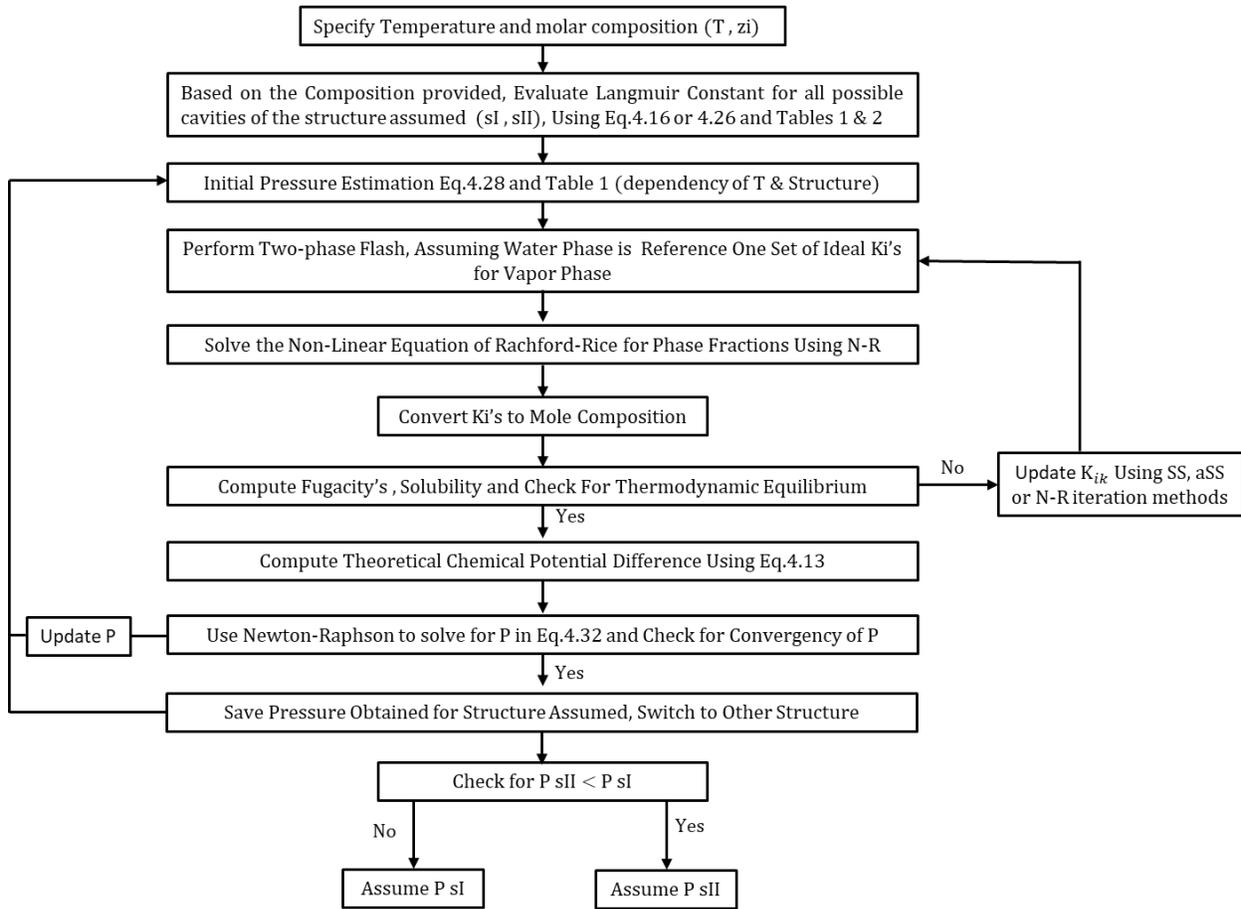


Figure 14 CSMHyd/ Modified Parrish and Prausnitz Algorithm for Hydrate dissociation Pressure (Second Locus of P-T diagram above ice point)

4.3.3 Improvement in Hydrate Modeling After Proposed Method of (Prausnitz W. 1972)

After the algorithm proposed by (Prausnitz W. 1972) who presented a detailed algorithm for (J.H.van der Waals 1959) for ice-hydrate-vapor and liquid water-hydrate-vapor phase equilibrium calculations in multi-component systems. In addition, the suggested two-parameter expression for the calculation of Langmuir constants that simplified the calculation of the Langmuir constants. Different modification and suggestion started to be implied to the algorithm or to original theory of vdW-P so to improve the accuracy of model prediction or to simplify the calculation.

The first simplification is (Holder 1988) equation (Eq. 4. 32) in which he eliminated the need for the reference pressure and thus simplified the calculations. After that (Jeffery B. Klauda 2000) presented a new explicit fugacity-based method for calculating gas hydrate equilibrium conditions. Their model was based on the original van der Waals-Platteeuw theory for the description of clathrate gas in the solid phase. However, the need for reference properties such as $\Delta H(T_0, P_0)$, $\Delta \mu(T_0, P_0)$ and $\Delta C_p(T)$ was removed in their approach. They stated that a large uncertainty in these reference properties are present since these values cannot be determined or measured for the

empty hydrate lattice. Despite that, the model was built in a way that instead of calculating reference chemical potential differences between a theoretical hydrate lattice and actual hydrate lattices, an actual fugacity of water in the hydrate lattice can be calculated directly. This fugacity was defined as the product of the water fugacity in the empty hydrate lattice, and the exponential to the (theoretical) chemical potential difference between the actual hydrate and the (pure) liquid water phase as following:

$$f_w^H = f_w^\beta \cdot \exp \left[\frac{-\Delta\mu_w^{\beta-H}}{R \cdot T} \right] \quad (4.33)$$

Where $-\Delta\mu_w^{\beta-H}$ is defined in Eq.4.5 or 4.8 while f_w^β was defined using Poynting factor by properties such as saturated water vapor pressure and its molar volume. Both of these properties were assumed temperature- and pressure dependent. In addition, (Jeffery B. Klauda 2000) attributed for the second and third water shells surrounding the guest in each cavity in the calculation of Langmuir constants. They claimed that model had not been “tuned” by fitting Langmuir parameters to actual hydrate dissociation pressure data but actually they were calculated from the Kihara cell potential with parameters found in the literature, where these had been estimated from gas phase viscosity data or second virial coefficients. In other words, no tune to the model is made since the measurement are accurate. In this study they have reported accurate prediction with a percent absolute average deviation in the predicted equilibrium pressures of 3.27% with two or three guest-hydrate specific parameters compared to more than 11% with three adjustable parameters in the vdW-P type models and 8.55% using a thermodynamic model that uses five guest-hydrate parameters for methane, ethane, propane, cyclopropane, iso-butane, carbon dioxide, nitrogen and hydrogen sulfide. Unlike (Jeffery B. Klauda 2000), (A.L Ballard 2002) suggested an improvement of the classical van der Waals- Platteeuw/Parrish-Prausnitz approach, but expanded the theory by accounting for the non-ideality of hydrate and including and accounting for lattice distortion in the form of an activity correction. In addition, (A.L Ballard 2002) proposed a new development of fugacity much simpler to use. Why we are discussing that? The hydrate model and the parameters presented by (A.L Ballard 2002) represent the approach adopted in CSMGem software.

4.4 Hydrate Model of Ballard 2002

(A.L Ballard 2002) Hydrate modeling carried out in CSMGem Software (Colorado School of Mineral)

4.4.1 Model Theory

(A.L Ballard 2002) Main modification was based on the fact that hydrates are non-ideal from a thermodynamic point of view. They stated that the current vdW-P hydrate model based on the statistical thermodynamics and classical thermodynamics is a good and acceptable model for moderate temperature and pressure conditions. However, as today’s need of energy became greater in which drilling and production is taking place from deep and ultra-deep water, the need for much more accurate model is necessary. Based on that, (A.L Ballard 2002) made an improvement to the

van der Waals and Platteeuw model in a way that it carries out the non-ideality of hydrates. The proposed modification to original vdW-P model hold the following two points:

- Activity coefficient for water in the hydrate account for the distortion of lattice structure.
- A new development of fugacity without the mandatory presence of an aqueous or ice phase so that fugacity of water of hydrate can be calculated in a standard thermodynamic sense.

4.4.1.1 Activity coefficient for water in hydrate

As it is mentioned in sections of this chapter that (J.H.van der Waals 1959) solution of the problem was based on splicing it into small problems. After that and by seeking solution for each spliced problem alone, they gave a solution for the real original problem (hydrate modeling). In other words, vdW-P followed up kind of three step engineering application to obtain the solution. However, in Step 3, we have showed that vdW-P made several assumptions so to be able to solve the problem. You don't recall Step 3? It is the application of adsorption theory so to involve the gas guest molecules into the theoretical/empty hydrate.

One major and questionable assumption was made in this step so to be able to use the necessary adsorption theory. This assumption concern that guest molecules does not distort the structural properties of the water lattice. Reformulating this sentence in simple words, while the guest (gas) molecule are adsorbed into the cavity of the empty hydrate, no change in the cavity volume is occurred. (A.L Ballard 2002) Didn't agreed about this assumption and considered that step 3 of the problem miss some physics. So, they added up to this step an activity coefficient that describe the distortion of the lattice structure together with the original physics made by vdW-P.

By accounting just for vdW-P physics in Step 3 (adsorption without the distortion of the water lattice or volume change), the only Gibbs free energy change is due to occupation of the hydrate cavities, as shown in Figure 15.

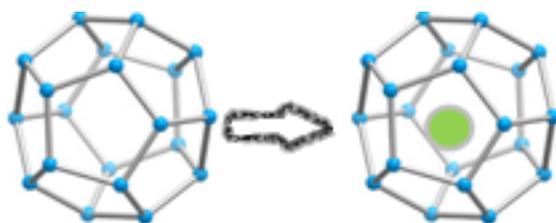


Figure 15 Original vdW-P not accounting for no distortion of lattice structure (produced)

By assuming that and looking to the equations we also realize that the chemical potential of the standard hydrate is at a given volume and independent of the hydrate guests. For simplicity, the idea of (A.L Ballard 2002) concerning the fact including the distortion is formulated in the following way/points:

- If the empty/theoretical hydrate volume is not equal to the volume of the actual hydrate at equilibrium, that mean additional energy change proportional to the difference in volume

should be added. How It can be added without reformulating the problem?

- Ans: add an activity coefficient account for the change of volume so to correct Gibbs free energy obtained by vdW-P theory.

(A.L Ballard 2002) Model is illustrated in the figure below

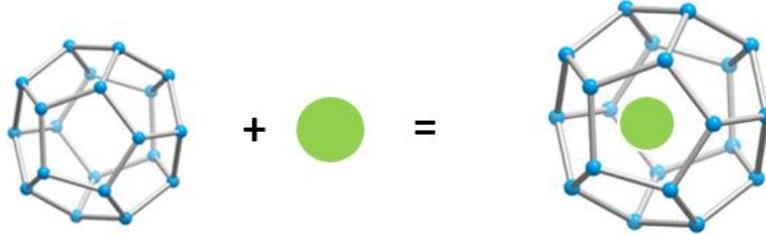


Figure 16 (A.L Ballard 2002) Modified model accounting for distortion of lattice structure (produced)

Rewriting Eq. (4. 5) for chemical potential difference between hydrate and empty hydrate and including the distortion term of Ballard and Sloan we obtain:

$$\Delta\mu(T, P, \theta)_w^{H-\beta} = R.T. \sum_m \left[v_m \cdot \ln \left(1 - \sum_j \theta(T, P, \bar{y})_{m,j} \right) \right] + \ln \gamma_{wH} \quad (4.34)$$

Where $\ln \gamma_{wH}$ is activity coefficient accounting for the perturbation of Gibbs energy due to volume change expressed as following:

$$\frac{\Delta_v g_{w\beta}}{R.T} = \frac{\Delta_v g_{w_0\beta}}{R.T_0} - \int_{T_0}^T \frac{\Delta_v h_{w\beta}}{R.T^2} dT + \int_{P_0}^P \frac{\Delta_v v_H}{R.T} \cdot dP \quad (4.35)$$

Where (A.L Ballard 2002) arbitrarily defined the perturbed potential or Gibbs energy and enthalpy of formation to be linear in ΔV^H such as $\Delta g_{w_0\beta} = a\Delta_v v_{H_0}$ and $\Delta_v h_{w_0\beta} = b\Delta_v v_{H_0}$ using parameters:

Table 5 Formation properties of empty hydrate

Hydrate	$g_{w_0\beta}$ (J/mole)	$h_{w_0\beta}$ (J/mole)	a (J/ cm3)	b (J/cm3)
sI	-235537.85	-291758.77	25.74	-481.32
sII	-235627.53	-292044.10	260.00	-68.64
sH	-235491.02	-291979.26	0	0

4.4.1.2 Fugacity development

(A.L Ballard 2002) Insisted that there is a major barrier in the fugacity equation of water in hydrate.

In order to compute fugacity of water in hydrate using Eq. (4. 33), firstly fugacity of water in empty hydrate need to calculate using:

$$f_w^\beta = f_w^{I/L} \cdot \exp \left[\frac{\Delta\mu_w^{\beta-I/L}}{R \cdot T} \right] \quad (4.36)$$

Where $f_w^{I/L}$ is the fugacity of pure ice or liquid water and $\Delta\mu_w^{\beta-I/L}$ is the difference in the chemical potential between the empty hydrate lattice and pure ice or liquid water.

The barrier described by (A.L Ballard 2002) is that in order to calculate the fugacity of water in hydrate (Eq.4.33), fugacity of ice or liquid water $f_w^{I/L}$ in (Eq. 4. 36) is required. In other words, an aqueous or ice phase must be present so to be able to calculate this fugacity while that is not always the case. Keep in mind that in order to check for thermodynamic equilibrium, the fugacity of water in the hydrate is necessary. To overcome this problem, (A.L Ballard 2002) combined Eq. (4. 33) and Eq. (4. 36) and reported the following expression for fugacity:

$$f_w^H = f_{wo} \cdot \exp \left[\frac{\Delta\mu_w^{\beta-H} - \Delta\mu_w^{\beta-I/L}}{R \cdot T} \right] \quad (4.37)$$

where

- f_{wo} is 1 bar
- $\Delta\mu_w^{\beta-I/L}$ is the chemical potential energy or equally Gibbs energy for pure water in the ideal gas state at 1 bar.

Remember that $\Delta\mu_w^{\beta-H}$ is calculated using Eq. (4. 34) not original Eq. (4. 5). Finally, and at the end of this section it is necessary to mention again that CSMGem (Colorado Scholl of mineral, Gibbs energy minimization) software carry out the model mentioned above for hydrate modeling together with Gupta's approach for stability analysis described in section 5.2.2.

4.4.1.3 Langmuir Constant

(Sloan ED 2008) Modified the integral limit of Langmuir constant proposed by vdW-P (Eq. 4. 15) and reported the following expression

$$C(T)_{m,j} = \frac{4 \cdot \pi}{k_B \cdot T} \cdot \int_0^{R_m - a_j} \exp \left[\frac{-w(r)_{m,j}}{k_B \cdot T} \right] \cdot r^2 \cdot dr \quad (4.38)$$

It is seen that the Kihara spherical core cell potential is undefined at $r = 0$. However, if one looks at the limiting value of the cell potential when approaching this from r values greater than zero, it may be shown that this point in the Kihara potential is a removable singularity. Also, $r = R_m - a_j$ a discontinuity with a change of sign occurs. Approaching $r = R_m - a_j$ from r values greater than this results in the cell potential approaching minus infinity making the behavior of the Langmuir adsorption coefficient divergent (Sloan ED 2008). Thus, care should have been taken, when

integrating the Kihara cell potential in CSMGem. Additionally, different optimized Kihara parameter have been used than the one reported by (Prausnitz W. 1972) and used in CSMHyd.

Table 6 Kihara Parameters reported by (Sloan ED 2008) used in CSMGem

Component	a_j (Å)	σ (Å)	ε/k (K)
Methane	0.3834	3.14393	155.593
Ethane	0.5651	3.24693	188.181
Propylene	0.6500	3.33039	186.082
Propane	0.6502	3.41670	192.855
n-Butane	0.9379	3.51726	197.254
i-Butane	0.8706	3.41691	198.333
i-Pentane	0.9868	3.54550	199.560
Nitrogen	0.3526	3.13512	127.426
Hydrogen Sulfide	0.3600	3.10000	212.047
Carbon Dioxide	0.6805	2.97638	175.405

4.5 MultiFlash and HydraFLASH® Hydrate Modelling

Hydrate modeling carried out in HydraFLASH® and MultiFlash Software

4.5.1 Model Theory

In both software, modeling of hydrates is based on the original vdW-P theory. However, this model is employed to calculate the fugacity coefficient of water in hydrate phase so to be used for thermodynamic equilibrium purposes. Both fugacity of water in hydrate and in empty hydrates are calculated and expressed in the same form as Eq. 4. 33 and 4. 36 respectively. In addition, Langmuir constant in HydraFLASH is calculated by adopting Eq. (4.38) with the following Kihara parameters (Tohidi-Kalorazi 1995) and used again in optimization of Kihara parameters for alcohols from the same institute in 2009 are as following:

Table 7 Kihara Parameters reported by (Tohidi-Kalorazi 1995) used in HydraFLAS

Component	a_j (Å)	σ (Å)	ε/k (K)
Methane	0.2950	3.2512	153.69
Ethane	0.4880	3.4315	183.32
Propane	0.7300	3.4900	189.27
i-Butane	0.7980	3.6000	209.58
n-Butane	1.0290	3.4000	210.58
Hydrogen Sulphide	0.7178	2.8770	210.58
Carbon Dioxide	0.7530	2.9040	171.97
Nitrogen, sI	0.3350	3.2171	128.39
Nitrogen, sII	0.3350	3.2690	134.08

Out of the scoop someone could ask here why we are reporting all Kihara parameters for every software and systems. The simplest answer that we can give at this step of the work is that it should be already clear until now that the theory of clathrates is not well developed and is based on experimental data fitting to optimize the prediction strength of the model. One of the major parameters that play a role in the prediction strength of a model may be Kihara parameter in which they are solely optimized parameters. In addition, the reference hydrate formation parameter has the same role. However, this study is a comparison study between different approaches and software, the outcome of which is to check the robustness of the approach/model. In other words, validation and strength of the already tuned model.

In addition to Kihara parameters of HydraFLASH reference hydrate structure parameters are obtained from (H.Haghighi 2009).

Table 8 Kihara Parameters reported by (H.Haghighi 2009) for ice co-existence phase used in HydraFLASH

Reference property	Structure I	Structure II
$\Delta\mu(T, P_R)_w^{\beta-Ice} / \text{J.mol}^{-1}$	1297	937
$\Delta H(T_0, P_0)_w^{\beta/Ice} / \text{J.mol}^{-1*}$	1389	1025
$\Delta V_w^{\beta/Ice} / \text{cm}^3.\text{mol}^{-1**}$	3.0	3.4

- In the liquid water region subtract 6009.5 J.mol⁻¹ from *
- In the liquid water region add 1.601 cm³ mol⁻¹ from **

And $\Delta C_p(T)$ in (Eq 4.26) is reported differently than (Prausnitz W. 1972) as following:

$$\Delta C_p(T) = -37.32 + 0.179(T - 273.15) \quad (4.39)$$

A very important Note: all hydrate models have more or less the same basis and they all rely on the theory of van der Waals- Platteeuw a good example of that is HydraFLASH and MultiFlash. However, what differentiates the strength of prediction from one to other is the tuning procedure and experimental data used. For example, and at this part of this work, we will give you a hint: one of the software/approaches could accurately predict in a specific locus of incipient hydrate dissociation (e.g. Lw-H-V) while in another locus it will poorly predict. Another approach could work in the opposite way while no change in basis theory is present. This fact can be explained on the fact that while tuning an approach frequent experimental data originally located in the same locus (good prediction) are used than any other. Why we are mentioning that? Here is a quick answer, data is money in our case the data are the experimental points used to tune and money is the business software present in the market. How that is related to the topic above? Kihara parameters and reference hydrate structure parameters are the Keys of increasing the balance amount of company's providing the software and since we are living in a capitalism world, no one will give you the key to gain money and sacrifice his own business or even to be in the danger zone of that. Based on that, unfortunately we haven't managed yet to obtain the Keys of KBC/MultiFlash Company. In other words, Kihara parameters and all other tuned parameters are still unaccusable. However, we will keep digging trying to find the keys.

Chapter 5

5 Thermodynamic Models

Studying thermodynamics of hydrates rigorously was initially attempted in 1959 by van der Waals and Platteeuw. This innovative study attempt initiated the process that led to the development of several tools/approaches enabling the analysis of complex systems (e.g. CO₂) later on. Nowadays, the approaches enable both understanding of hydrates and the efficient development in flow assurance in the oil and gas industries. In their model, VdW-P took advantage of Langmuir adsorption theory to describe guest molecules adsorption in a theoretical empty hydrate. While some of the approaches present today adopted the original theory of vdW-P, others, questioned an assumption present in the theory basis. This assumption describes guest molecules adsorption in the empty theoretical hydrate (defined by VdW-P). In this, it is stated that guest molecules make no distortion of the theoretical empty hydrate lattice structure. (A.L Ballard 2002) eliminated this questionable assumption by adding an activity coefficient to the original theory of VdW-P. The activity coefficient covers only the distortion factor in the empty hydrate structure. On the other hand, different approaches took advantage of the ability of CPA (Cubic Plus Association) EoS in modeling hydrogen bonding. Others use simple cubic EoS (e.g. SRK) to model polar components (e.g. water). Additionally, in each of these approaches, several thermodynamic tools have been used for different descriptions of different possible hydrates co-existing phases (e.g. ice).

In Chapter 2, the formulation of a phase equilibria problem using Two and Multiphase systems is shown. The first outcome of which is that material balance (M.B) and thermodynamics are combined to describe the real problem. Typically, the thermodynamic constraint is satisfied or respected when all fugacity of each component at all phases are equal.

In Chapter 4, the fugacity calculation of water in hydrates is discussed in detail. In other words, the fugacity model of water in hydrate is already present. But what about other phases (vapor, ice...)? In the procedure explained in Chapter 2, it is assumed that the tools and relationships of different models used to check for thermodynamic equilibrium exist. If so, what are these tools and how they are correlated to the intensive properties of interest?

In this chapter, the discussion will be mainly based on different thermodynamic models and auxiliary functions used to simplify Gibbs equations for equilibrium (e.g. fugacity, activity coefficient). Keeping in mind that this study is a comparison between different software/approaches, so it is evident to know each approach or software adopted models for each phase treatment and calculation. With that, a better understanding of the algorithm behavior in each software will be decelerated. Consequently, a much accurate analysis of results can be made. Based on that, the end of this chapter will be providing a summary of this information.

In a typical petroleum system and under the assumption that the system will split and form more than one phase at equilibrium, vapor gas hydrocarbons, and liquid hydrocarbons will be present.

However, in some rare cases of high carbon dioxide concentration and due to the non-ideal behavior of this component, carbon dioxide can be present in both liquid and vapor phases. Additionally, the hydrate system at equilibrium may be formed with several co-existent phases such as Ice, Liquid water, vapor hydrocarbons, and liquid hydrocarbons. Also, other phases and components can be present in hydrate such as salts, alcohols, glycols. In a typical industrial case, both alcohols and salts can be present simultaneously. The last case can be present in a system of a pipeline connecting directly offshore gas production to the onshore. Offshore gas platforms are limited space platforms so while producing gas and especially in cases of huge reserves (e.g. Offshore Zohr Egypt), due to the limited spaces of platforms no storage of produced gas will take place. The gas will be directly sent onshore through a pipeline. However, since gas stream trajectory start from the reservoir following well-pipes to transport pipelines and keeping in mind that the gas is produced from reservoir formation in which saline water is present (average order of 350,000 ppm) while no treatment of water that will take place at the platform, a significant (Water-aquifers presence) to negligible amount of saline water is present within the gas phase in pipeline. Based on this fact, the only remained solution to avoid the risk of hydrate blockage, in this case, is thermodynamic inhibitors injection. As a conclusion, the typical (real-life) industrial case will include salts, alcohols, vapor hydrocarbons and probably liquid hydrocarbon too in a state of high concentration of light components and finally aqueous phase. Thus it is essential to know how to model each phase that may be present in the system.

What has been stated conclude the major objective of this chapter. However, at this point, this chapter will present the major tools for the main phases of forming hydrates where salts and inhibitors' models will not be explained. Salts (Electrolytes) modeling and inhibitors will be explained separately in a different chapter within the results of this study for each mentioned phase.

Fugacity was defined by the thermodynamics G. N. Lewis, this property is better understood by engineers and physically felt than abstraction chemical potential. We have used fugacity to get around the mathematical anomalies faced in solving the phase equilibria problem. Fugacity is defined inductively while other thermodynamic parameters are defined deductively. For example, enthalpy is developed by combining internal energy and flow work of the system while fugacity definition started with an ideal/real gas which later is extended to the liquid and solid phase. Fugacity is the parameter that replaced pressure due non-ideality of molecules of the phase. It is known that intermolecular forces of gases cause deviations of the gas from ideality, in which the behavior is called real gas behavior. To describe ideal gas, fugacity and pressure both can be used correspondingly while in real gas systems, only fugacity is used.

5.1 Vapor Phase

Reliable thermodynamic data is required in advance to obtain fugacity for pure real gas through thermodynamic tables, equation of state or generalized correlations. For the need of one fugacity value, fugacity tables are the best method to be used where thermodynamic tables are based on reliable experimental work. However, that is not the case in this problem (Hydrate, Petroleum). In reality and both areas, we don't expect to encounter a pure real gas. Additionally, in different

algorithm sections, iteration techniques are required to achieve the correct answer or the global minimum of Gibbs energy thus the table's values cannot be relied on.

For any engineer, algorithm scientist or software engineer a relationship that correlates fugacity to all dependent parameters would be ideal. This relationship is provided by the use of already present cubic EoSs. However, to use EoS in obtaining fugacity-coefficient for a component i in a mixture, the need to describe PvT Property's behavior for that mixture is necessary. Unlike pure components which are described experimentally, the need for mixture rules such as van-der-Waals rules is the only solution to overcome this problem.

The theoretical justification of mixture rules is so limited. A mixture rule works perfectly in describing a certain mixture or fluid while for another one is not necessarily true. Despite that now, this work does not involve studying the effect of mixture rules on the prediction of our models/approaches.

Starting by Eq. (2. 5)

$$\mu_i - \mu_i^0 = RT \ln \left[\frac{\hat{f}_i}{f_i^0} \right]$$

where

- μ_i is the chemical potential for pressure, temperature, and composition of interest.
- μ_i^0 is the chemical potential for chosen reference at the same temperature and composition of the mixture at low pressure (this one is criteria for the definition of fugacity and is discussed down why such a reference state is chosen).

To correlate fugacity within an EoS, the partial derivative relation of Gibbs energy is substituted in Eq. (2. 5)

$$\mu_i - \mu_i^0 = \int_{P_{low}}^P \bar{V}_i dP = RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{low}} \right] \quad (5.1)$$

For detailed substitution search for "Relations among Partial Molar Quantities". By looking at Equation 5.1, a volume explicit equation of state is required. This is not the case with typical EoS where they are pressure explicit equations. To overcome this issue, Eq. (5. 1) is to be rewritten so that to use typical pressure explicit EoS. To do so first recalling the definition of partial molar property

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (5.2)$$

using the well-known cyclic rule at constant T

$$\left(\frac{\partial V}{\partial n_i} \right)_{T,P} \left(\frac{\partial P}{\partial V} \right)_{T,n_i} \left(\frac{\partial n_i}{\partial P} \right)_{T,V} = -1 \quad (5.3)$$

Since we have chosen the reference phase to be identical in temperature and composition, cyclic rule in Eq. (5. 3) can be written as:

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P} dP = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V} dV \quad (5.4)$$

substituting (5. 4) into (5. 1)

$$RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{low}} \right] = - \int_{\left(\frac{n_T RT}{P_{low}}\right)}^V \left(\frac{\partial P}{\partial n_i}\right)_{T,P,n_{j \neq i}} dV \quad (5.5)$$

Finally, using Eq. (5. 5) fugacity is formulated within a cubic pressure explicit EoS.

Note: In this work, it is purposely avoided discussing the fundamentals of thermodynamic to keep the track mainly and solely from an engineering point of view.

Obtaining Eq. (5. 5) and by choosing a reliable cubic equation of state, describing the fugacity explicitly is now much easier. Several cubic equations of state (EoS) are used in both areas hydrate and petroleum for vapor phase treatment. However, the two well-known equations of state for which several publications came out and dozens of the authors agreed on are Peng Robinson (PR-EOS-1976) and Soave-Redlich-Kwong (SRK-EoS-1972) which give the best prediction in petroleum field (e.g. VLEP). One of these two equations can be chosen for the calculations needed. Additionally, this study involves the effect of cubic EoS type on hydrate prediction in which until now no one has studied/reported this effect. At this phase, to this point, just a general idea of EoS has been given. However, this study includes the effect of EoS choice on hydrate prediction accuracy, a short description of cubic EoS will be given later. At this stage of the calculations and for simplicity reasons, van-der-Waals equation of state with simple mixture rules are chosen to describe obtaining explicit fugacity relationship, using EoS as following:

$$P = \frac{RT}{v - b_{mix}} - \frac{a_{mix}}{v^2} \quad (5.6)$$

where

- a_{mix} Is the attraction term covers the intermolecular forces between molecules and is dependent on the gas molecules present.
- b_{mix} Is the co-volume excluded term and is related to the size of molecules.

As it is mentioned above that each of the parameters is related to a specific molecule. When it comes to mixtures simple mixture rules are assumed since no molecular theory can describe mentioned parameters for mixtures. Using qualitative molecular description combined with mathematical simple averaging van-der-Waals proposed the following description of 2 mixtures (a and b):

$$a_{mix} = \sum \sum y_i y_j a_{ij} \quad (5.7)$$

in which

$$a_{ij} = \sqrt{a_{ii} a_{jj}} \quad (5.8)$$

where

- a_{ii} represents the attraction between like i molecules
- a_{ij} represents the interaction between one i molecule and one j molecule, the unlikely interaction.

However, when more data are present the empirical fitting parameter k_{ij} is obtained for better prediction.

$$a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (5.9)$$

In some cases, this binary interaction parameter is used as a tuning parameter for better prediction of EoS and a better prediction of reservoir fluid PvT properties.

For the size b_{mix} parameter, it is most convenient to average molecular volumes as follows:

$$b_{mix} = \sum y_i b_i \quad (5.10)$$

Now after discussing all of this let's go back to Eq. (5. 5) and derive an equation for fugacity using Eq. (5. 6).

For more simplicity, let's assume a binary mixture compound of components a and b. Starting by rewriting Eq. (5. 5) for the binary mixture described

$$RT \ln \left[\frac{\hat{f}_a^v}{y_a P_{low}} \right] = - \int_{\left(\frac{n_T RT}{P_{low}}\right)}^V \left(\frac{\partial P}{\partial n_a} \right)_{V,T,n_b} dV \quad (5.11)$$

rewriting Eq. (5. 6) for the same mixture

$$P = \frac{RT(n_a + n_b)}{V - (n_a b_a + n_b b_b)} - \frac{n_a^2 a_a + 2n_a n_b \sqrt{a_a a_b} + n_b^2 a_b}{v^2} \quad (5.12)$$

in addition to Eq. (5. 7), (5. 10)

$$a_{mix} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b \quad (5.13)$$

$$b_{mix} = y_a b_a + y_b b_b \quad (5.14)$$

and applying the mass balance

$$n_T = n_a + n_b \quad (5.15)$$

deriving (5. 12)

$$\left(\frac{\partial P}{\partial n_a}\right)_{T,V,n_b} = \frac{RT}{V - (n_a b_a + n_b b_b)} + \frac{b_a RT(n_a + n_b)}{[V - (n_a b_a + n_b b_b)]^2} - \frac{2(n_a a_a + n_b \sqrt{a_a a_b})}{V^2} \quad (5.16)$$

substituting (5. 12) into (5. 11)

$$\ln \left[\frac{\hat{f}_a^v}{y_a P_{low}} \right] = -\ln \left[\frac{V - n_T b_{mix}}{\left(\frac{n_T RT}{P_{low}}\right) - n_T b_{mix}} \right] + \frac{b_a(n_a + n_b)}{[V - n_T b_{mix}]} - \frac{b_a(n_a + n_b)}{\left[\left(\frac{n_T RT}{P_{low}}\right) - n_T b_{mix}\right]} - \frac{2(n_a a_a + n_b \sqrt{a_a a_b})}{RTV} + \frac{2(n_a a_a + n_b \sqrt{a_a a_b})}{RT \left(\frac{n_T RT}{P_{low}}\right)} \quad (5.17)$$

Simplification can be made to Eq. (5.17) on the following basis $\frac{RT}{P_{low}} \gg b_{mix}$, adding $\ln(P_{low})$ to both sides and considering that P_{low} tends to 0, Eq (5.17) becomes:

$$\ln \left[\frac{\hat{f}_a^v}{y_a} \right] = -\ln \left[\frac{(V - n_T b_{mix})}{n_T RT} \right] + \frac{b_a(n_a + n_b)}{[V - n_T b_{mix}]} - \frac{2(n_a a_a + n_b \sqrt{a_a a_b})}{RTV} \quad (5.18)$$

Subtracting $\ln(P)$ from both sides' leaves:

$$\ln \left[\frac{\hat{f}_a^v}{y_a P} \right] = \ln[\hat{\varphi}_a^v] = -\ln \frac{P(v - b_{mix})}{RT} + \frac{b_a}{[v - b_{mix}]} - \frac{2(y_a a_a + y_b \sqrt{a_a a_b})}{RTv} \quad (5.19)$$

An explicit equation of fugacity using cubic EoS correlating all intensive properties of interest is already formulated. The following table summarizes the fugacity coefficient for three cubic equatio

Table 9 Fugacity coefficient for three cubic EoS

Van der Waals	
Equation of state	
Pure component i	$\ln \varphi_i = \frac{b_i}{v_i - b_i} - \ln \left(\frac{(v_i - b_i)P}{RT} \right) - \frac{2a_i}{RTv_i} \quad (5.20)$
Component i in a binary mixture.	$\ln \widehat{\varphi}_1 = \frac{b_1}{v - b} - \ln \left(\frac{(v - b)P}{RT} \right) - \frac{2(y_1 a_1 + y_2 a_{12})}{RTv} \quad (5.21)$
Species i in a mixture	$\ln \widehat{\varphi}_i = \frac{b_i}{v - b} - \ln \left(\frac{(v - b)P}{RT} \right) - \frac{2 \sum_{k=1}^m y_1 a_{ik}}{RTv} \quad (5.22)$
Redlich-Kwong	
Equation of State	
Pure component	$\ln \varphi_i = z_i - 1 - \ln \left(\frac{(v_i - b_i)P}{RT} \right) - \frac{a_i}{b_i RT^{1.5}} \ln \left(1 + \frac{b_i}{v_i} \right) \quad (5.23)$
Component i in a binary mixture	$\ln \widehat{\varphi}_1 = \frac{b_1}{b} (z - 1) - \ln \left(\frac{(v - b)P}{RT} \right) + \frac{1}{b RT^{1.5}} \left[\frac{ab_1}{b} - 2(y_1 a_1 + y_2 a_{12}) \right] \ln \left(1 + \frac{b}{v} \right) \quad (5.24)$
Species i in a mixture	$\ln \widehat{\varphi}_i = \frac{b_i}{b} (z - 1) - \ln \left(\frac{(v - b)P}{RT} \right) + \frac{1}{b RT^{1.5}} \left[\frac{ab_i}{b} - 2 \sum_{k=1}^m y_1 a_{ik} \right] \ln \left(1 + \frac{b}{v} \right) \quad (5.25)$
Peng Robinson	
Equation of State -	
Pure component i	$\ln \varphi_i = z_i - 1 - \ln \left(\frac{(v_i - b_i)P}{RT} \right) - \frac{(a\alpha)_i}{2\sqrt{2}b_i RT} \ln \left[\frac{v_i + (1 + \sqrt{2})b_i}{v_i + (1 - \sqrt{2})b_i} \right] \quad (5.26)$
Component 1 in a binary mixture	$\ln \widehat{\varphi}_1 = \frac{b_1}{b} (z - 1) - \ln \left(\frac{(v - b)P}{RT} \right) + \frac{a\alpha}{2\sqrt{2}b RT} \left[\frac{b_1}{b} - \frac{2}{a\alpha} (y_1 (a\alpha)_1 + y_2 (a\alpha)_{12}) \right] \ln \left[\frac{v + (1 + \sqrt{2})b}{v + (1 - \sqrt{2})b} \right] \quad (5.27)$
Species i in a mixture	$\ln \widehat{\varphi}_i = \frac{b_i}{b} (z - 1) - \ln \left(\frac{(v - b)P}{RT} \right) + \frac{a\alpha}{2\sqrt{2}b RT} \left[\frac{b_i}{b} - \frac{2}{a\alpha} \sum_{k=1}^m y_k (a\alpha)_{ik} \right] \ln \left[\frac{v + (1 + \sqrt{2})b}{v + (1 - \sqrt{2})b} \right] \quad (5.28)$

5.2 Liquid Hydrocarbon Phase

It should be clear that thermodynamic equilibrium is achieved when all components' fugacity values in different phases present are equal. In other words, the component tendency of escaping is the same in all phases. However, in the last section (5. 1), a detailed description is presented on the way of obtaining the fugacity or fugacity coefficient for components present in the vapor phase using EoS. Based on that a part of the problem is already solved regarding the vapor phase.

Now considering the liquid phase, a summarized equation for fugacity coefficient can be used to describe it in this state

$$\ln \varphi_i = \ln \gamma_i + \ln p_i^{sat} + \ln \varphi_i^{sat} - \ln p + \Pi_i \quad (5.29)$$

where

- φ_i is the fugacity coefficient of interest i .
- γ_i is the activity coefficient of component i .
- p_i^{sat} is the saturated vapor pressure of component i .
- p is the total pressure.
- Π_i is Poynting correction.

in which $\ln \gamma_i$ is derived from the Excess Gibbs energy as follows:

$$\ln \gamma_i = \frac{\partial G^E}{\partial n_i} \quad (5.30)$$

However, the excess Gibbs energy at this stage of this work is not considered since EoS models are used to calculate fugacity and not EoS with an activity coefficient. In other parts of this work where salts/inhibitors are present, this term is necessarily tested in some approaches. In the hydrocarbon liquid phase, this term is eliminated. The remained parts of the equation can be explained using the knowledge already known for a petroleum engineer. To explain a P- v diagram is illustrated.(Figure 18).

Considering the equality of fugacity at equilibrium condition and applying that to the isotherm line at saturation pressure

$$f_l^{sat} = f_v^{sat} \quad (5.31)$$

This equation is true for the blue points in the P- v diagram of a pure component at constant temperature and pressure. But regarding the Fugacity of liquid, it is obtained at a pressure p_i (red point) through extrapolating fugacity value of the saturated liquid point (this part regarding liquid phase fugacity is yet to be proved).

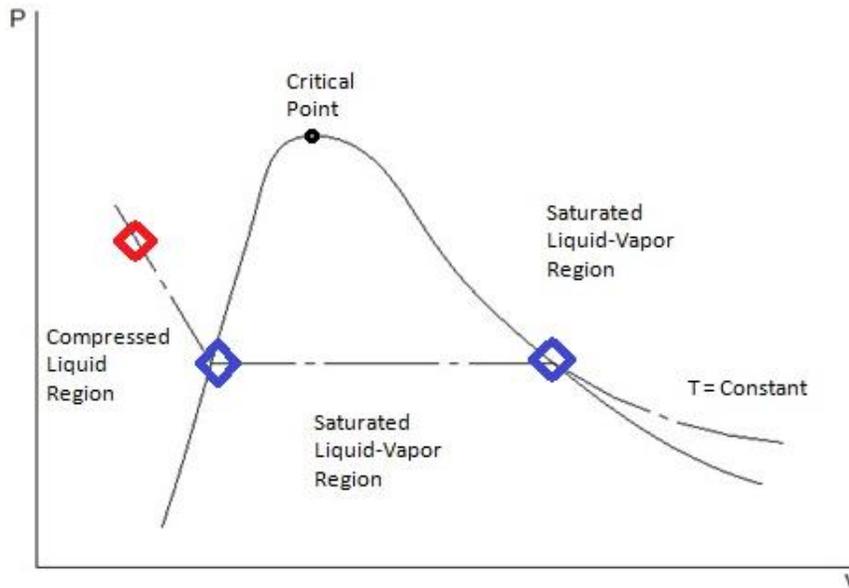


Figure 18 P-v diagram of a pure component

Rewriting fundamental Gibbs energy Equation (4. 21) for isothermal compression process

$$dG = VdP \quad (\text{const } T) \quad (5.32)$$

Integrating Eq. (5. 32) between pressure p_i and p_i^{sat}

$$G_i - G_i^{sat} = \int_{p_{sat}}^P V_i dP \quad (5.33)$$

Defining Gibbs energy for different state

$$G_i(p_i) = [T) + RT \ln f_i \quad (5.34)$$

&

$$G_i^{sat}(p_i^{sat}) = [T) + RT \ln f_i^{sat} \quad (5.35)$$

Where $[T)$ is constant for the reference chosen (it is free to use any reference phase under some conditions mentioned before). Despite that, Subtracting Eq. (5. 34) from (5. 35) and substituting into (5.33) results in

$$RT \ln \frac{\ln f_i}{\ln f_i^{sat}} = \int_{p_i^{sat}}^P V_i dP \quad (5.36)$$

Rearranging Eq. (5.36) to obtain fugacity f_i at the pressure of interest p_i

$$f_i = f_i^{sat} \exp \frac{\int_{p_i^{sat}}^P V_i dP}{RT} \quad (5.37)$$

And assuming reservoir fluid (a slightly to incompressible fluid) V_i can be assumed constant with pressure thus Eq. (5.37) can be written as

$$f_i = f_i^{sat} \exp \frac{V_i(P - p_i^{sat})}{RT} \quad (5.38)$$

Replacing f_i^{sat} by $\phi_i^{sat} p_i^{sat}$ so to understand each term in Eq. (5.29)

$$f_i = \phi_i^{sat} p_i^{sat} \exp \frac{V_i(P - p_i^{sat})}{RT} \quad (5.39)$$

Comparing Eq. (5.39) to (5.29) leads to

$$\Pi_i = \frac{V_i(P - p_i^{sat})}{RT} \quad (5.40)$$

To understand the behavior of Poynting correction factor and water Poynting factor at different pressure and temperature values for water the results in hand are illustrated in the following graph:

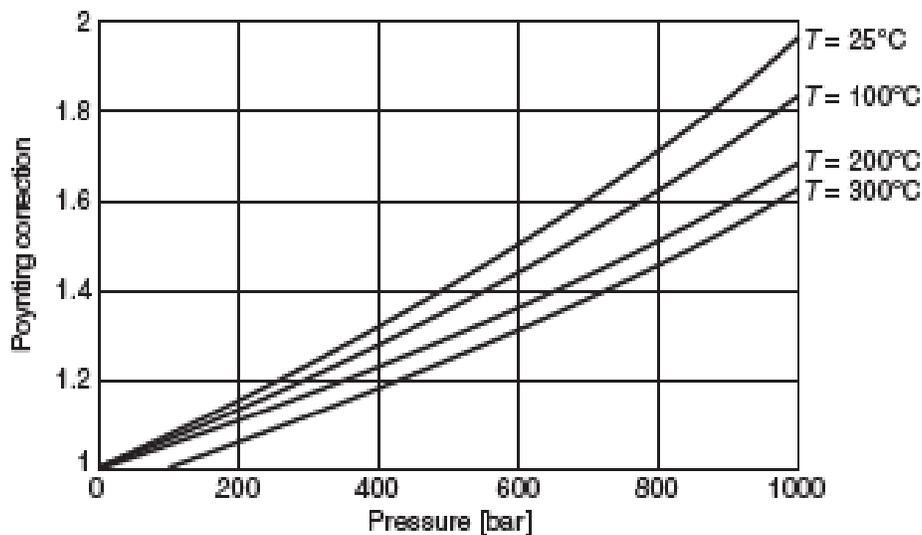


Figure 19 V Poynting correction factor for water (pressure and temperature effect) (M. D. Koretsky n.d.)

As shown in figure 5.2 that Poynting correction factor at high pressure and low temperature may double the value of fugacity. However, at low pressure, Eq. (5.39) can be simplified

$$f_i = \phi_i^{sat} p_i^{sat} \quad (5.41)$$

And at low pressure, the gas will behave as an ideal gas and the fugacity of components is equal to saturation pressure.

Very Important Note: fugacity calculations are shown using cubic EoS both for gas and liquids just to review and have the way of thinking of a petroleum engineer that deals only with cubic EoS and mostly VLE problems. However, in hydrates this not what we use! How is that? Dealing with EoS models for hydrates is slightly more complicated. What is additional? The answer to this question starts by reminding our self what phases are present in hydrates. Vapor gas, liquid hydrocarbons, ice, and aqueous phase. More details required? Firstly, remember that a typical case of natural gas reservoir fluid includes impurities. Before working with hydrates and reading this work you may didn't know why the presence of impurities (e.g. CO₂) increase the deviation of PvTData predicted by an EoS from experimental data produced in the laboratory. But after doing so and reading carefully Chapter 3 (CPA equation of state) you understood the polarity of molecules and the need of an EoS that cover hydrogen bonding, cross association and self-association is necessary. However, as all petroleum engineers know that simple EoS are only used in petroleum engineering fields Now you may be asking yourself how simple cubic EoS can cover and predict reservoir fluid with impurities? How we rely and we have been relying on it? The simplest answer is we don't rely on EoS simply, we tune it so to predict as close as possible the reservoir fluid of interest. Why we are mentioning that? To make the idea physically understood for a way of thinking of any petroleum engineer reading this work. After understanding the impurities effect in petroleum engineering, please add to now water, alcohols or salts that in most cases they are present. Keep that in mind and try to think using which equation of state we should start an algorithm for hydrate with all mentioned case? Remember that you do have one full algorithm for hydrates that should be able to model any type of fluid. The logical answer is start always with CPA. Introduce to your algorithm all necessary data that is needed to calculate the association term for all cases that you encounter in hydrates (e.g. CO₂, inhibitors etc.). By doing so the algorithm will start always with full CPA EoS, this is used across gas, liquid and aqueous phase. However, the association term is really active only for polar components and therefore the energy term reduces or eliminates directly for non-polar (e.g. methane, butane) due to no value is present or entered for CPA association term calculation so to include just the original (Cubic term), for non-polar components. In other words, the CPA for non-polar component is reduced back to simple cubic EoS (PR, SRK etc.). Thus, fugacity is calculated in the same way described in the chapter sections above. Conclusion: if CPA EoS is chosen for modeling and calculating fugacity in hydrates, the association term is always there, thus if you have methanol or MEG for instance, or CO₂, it becomes relevant in gas and liquid phase as well.

Based on what is mentioned in the note above, fugacity calculation using CPA equation of state is

described below:

Recalling Eq. (5. 5)

$$RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{low}} \right] = - \int_{\left(\frac{n_T RT}{P_{low}}\right)}^V \left(\frac{\partial P}{\partial n_i} \right)_{T,P,n_{j \neq i}} dV \quad (5.42)$$

To substitute CPA EoS in the integral, Eq. (3. 1), (3. 2) and (3. 3) should be written explicitly in pressure. As a summary of all equations mentioned CPA EoS can be written

$$P^{sys} = P^{Cubic} + P^{Association} \quad (5.43)$$

$$P^{sys} = \frac{RT}{V_m - b} - \frac{a_0 \propto (T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln(g)}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X^{A_i}) \quad (5.44)$$

Same as fugacity calculation presented for a cubic EoS (sections 5.1-5.2), the association term is represented using the simplified equations reported by (Michelsen M.L. 2001)

$$\frac{\partial}{\partial n_i} \left(\frac{A^r_{association}}{RT} \right) = - \sum_{A_i} \ln X_{A_i} + \frac{h}{2} \frac{\partial \ln g}{\partial n_i} \quad (5.45)$$

$$h = \sum_i n_i \sum_{A_i} (1 - X_{A_i}) \quad (5.46)$$

and

$$\frac{\partial \ln g^{simp.}}{\partial n_i} = \frac{0.475B}{V - 0.475B} \quad (5.47)$$

5.3 Ice Phase

As all solid phases, thermodynamics provide a different way to model the ice phase. In this section, only the method used in different approaches of this study for treating the ice phase will be discussed. The simplest way of modeling ice is by calculating the fugacity of ice using classical thermodynamic treatment. Other ways include the usage of Poynting correction for which fugacity of water in the vapor phase at the specified pressure first, after that using the Poynting correction factor explained in section 5.2 but for ice phase so to correct/extrapolate the fugacity to be valid for ice. Another method to do so is using the solid freeze-out method. The application of these methods is explained briefly as following.

5.3.1 Classical Thermodynamic Treatment

The fugacity of ice is calculated using classical thermodynamic treatment

$$f_{i,s} = f_{i,o} \exp \left[\frac{g_{i,s} - g_{i,o}}{RT} \right] \quad (5.48)$$

where

- $f_{i,o}$ refers to the property if component i in the ideal gas state.
- $g_{i,s}$ is Gibbs energy of component i in a solid phase.
- $g_{i,o}$ is Gibbs energy of component i in the ideal gas state
- $g_{i,s}$ is given by

$$\frac{g_{i,s}}{RT} = \frac{g_{i,o,s}}{RT_0} - \int_{T_0}^T \frac{h_{i,s}}{RT^2} dT + \int_{P_0}^P \frac{V_{i,s}}{RT} dP \quad (5.49)$$

However, since there is only one component in the pure solid phase (ice), all other components are assumed to have an infinite fugacity in the pure phases.

5.3.2 Poynting Correction Method

The fugacity of ice is calculated using the Poynting correction on the same basis that was shown in section 5.2 via the following equation provided by (HydraFLASH n.d.)

$$f_w^l = \phi_w^{Sat} P_I^{Sat} \exp \left(\frac{v_I (P - P_I^{Sat})}{RT} \right) P \quad (5.50)$$

where

- f_w^l is the fugacity of water in the ice phase
- ϕ_w^{Sat} is the fugacity coefficient of water in the vapor phase at the specified pressure
- v_I is the ice molar volume
- P is the vapor pressure of ice

in which

$$v_I = 19.629 \cdot 10^{-6} + 2.2364 \cdot 10^{-9}(T - 273.15) \quad (5.51)$$

$$\ln\left(\frac{P_I^{Sat}}{P_n}\right) = a_1(1 - \theta^{-15}) + a_2(1 - \theta^{-125}) \quad (5.52)$$

$$a_1 = -13.9281690 \quad (5.53)$$

$$a_2 = 34.7078238 \quad (5.54)$$

$$P_n(Pa) = 611.657 \quad (5.55)$$

$$T_n(K) = 273.16 \quad (5.56)$$

5.3.3 Solid Freezeout-Model

This method works on the following basis: it states that while solving for a thermodynamic phase equilibrium for hydrates, a solution for other phases with gas, hydrocarbon liquid, aqueous and gas hydrate phases (sI, sII, sH) must be sought for simultaneously, it is of a major importance to ensure achieving the correct solution of phase equilibrium and thermodynamic validity. Based on that and to model pure solid formation that may be present as ice or solid CO₂ purely, it strongly depends on the thermal properties of an individual component, such as melting point temperature, enthalpy of fusion and volume change due to. Taking all that has been mentioned into consideration and to assure that solid freeze-out model works for any component present in that model, the following equation with already known thermal properties reported by (KBC n.d.) Is given as:

$$\ln \phi_i = \ln \phi_i^{liq} - \left(\frac{\Delta H - T_{ref} \Delta C_p}{R}\right) \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) + \frac{S_{corr}}{R} + \frac{\Delta C_p}{R} + \ln\left(\frac{T}{T_{ref}}\right) - \frac{(p - p_{atm}) \Delta V}{RT} \quad (5.57)$$

where

- ϕ_i refers to the fugacity coefficient of pure solid component i
- ϕ_i^{liq} is the fugacity coefficient of the same component as a pure liquid at the same pressure P and temperature T (it is calculated from the liquid phase model associated with the freeze-out model)
- ΔH , ΔC_p and ΔV are the changes in molar enthalpy, molar heat capacity, and molar volume respectively on fusion at the melting point
- T_{ref} is a reference temperature that corresponds to the normal melting point when $S=0$ which is assumed in this case.
- p_{atm} is atmospheric pressure.

ΔH , ΔC_p and ΔV are constants and while this method is adopted in this approach they are introduced in advance as physical property data source. By doing so and defining general models like the Solid-Freezeout model methane, carbon dioxide, and water that might be present in hydrate cases as solid can be modeled.

5.4 Aqueous Phase

Although it is known that gases present in hydrate cases are poorly soluble in water (e.g. CO₂, CH₄) however, the fugacity of this component in aqueous phase should be taken into consideration so to ensure accurate phase equilibria solutions. Additionally, the fugacity of water in the aqueous phase needs to be obtained for the Gibbs energy minimization procedure needed in the algorithm. This part will be stating different ways of fugacity calculation for different components that may be present in an aqueous phase, and concluding results regarding the other models used for water in the aqueous phase in the approaches tested within this study.

5.4.1 Fugacity Models for Dissolved Gas

In this part, different models adopted in different approaches will be described briefly for fugacity calculations of components in the aqueous phase.

5.4.1.1 Classical Thermodynamic Treatment

Fugacity of any component in the aqueous phase can be expressed in a thermodynamic sense using the following equation

$$f_{i,o} e f_{i,Aq} = xp \left[\frac{\mu_{i,Aq} - g_{i,o}}{RT} \right] \quad (5.58)$$

where

- $f_{i,o}$ and $g_{i,o}$ refers to the property of component i in the ideal gas state.
- $\mu_{i,Aq}$ the chemical potential of component i at the specified temperature and pressure.

in which

$$\frac{\mu_{i,Aq}}{RT} = \frac{\mu_{i,**}}{RT} - \int_{T_0}^T \frac{\bar{h}_{i,**}}{RT} dT + \int_{P_0}^P \frac{\bar{V}_{i,**}}{RT} dP + \ln a_{i,Aq} \quad (5.59)$$

** refers to component i in a hypothetical 1 molar solution.

5.4.1.2 Eos Model

In sections before it was shown how to calculate fugacity by mean of EoS. Also, an important note

has been written in the text state that in all approaches where EoS model has been used, the algorithm or the calculation always start using a CPA EoS, in which when polar components are encountered in any phase, the association term of CPA will be active while it is not in other cases. Similarly, in an aqueous phase, for dissolved polar components gas (e.g. CO₂), fugacity is calculated within a complete CPA EoS (association term present) while for non-polar gas components (e.g.) the association term is eliminated directly.

5.4.2 Fugacity Models for Water

Following the same procedure, this section describes briefly different models adopted in different approaches for fugacity calculation of water component in the aqueous phase.

5.4.2.1 Classical Thermodynamic Treatment

Fugacity of water in the aqueous phase can be expressed in a thermodynamic sense similarly to Eq. (5. 48) as following

$$f_w^{Aq} = f_{w0} \cdot \exp \left[\frac{\mu_{w,Aq} - g_{w0}}{R \cdot T} \right] \quad (5.60)$$

where

- f_{w0} and g_{w0} refers to the property of water in the ideal gas state (1 bar).
- $\mu_{w,Aq}$ Is the chemical potential of water at the specified temperature and pressure.

in which

$$\frac{\mu_{w,Aq}}{RT} = \frac{g_{w0,*}}{RT_0} - \int_{T_0}^T \frac{h_{w,*}}{RT^2} dT + \int_{P_0}^P \frac{V_{w,*}}{RT} dP \quad (5.61)$$

** refers to the pure liquid water phase.

Keep in mind what was mentioned at the beginning and in different sections of this chapter. The main objective of this chapter is to make the reader familiar with different models used in different approaches for all cases except systems where salts and inhibitors are not present. The extension of this model for the remaining cases will be discussed in other parts of this work. At this stage, for cases where salts (electrolytes) are present in the system and for cases where the classical thermodynamic model is used, an additional term is needed, the activity coefficient term.

5.4.2.2 Eos Model

This section is just to clarify for the reader the already described point that by the usage of EoS

models for fugacity calculations, all approaches tested use CPA EoS. Since water is considered a weakly-polar component in which microscopical hydrogen bonding (self-association) needs to be described, the association term is always active for water case. Based on that and as water is present in all the phases (e.g. vapor) fugacity is calculated within CPA EoS. For a full description of the fugacity model using CPA EoS, refer to section 5.1.

Chapter 6

6.1 Approaches Application

The main objective of this study is to provide the oil and gas industry with answers about the accuracy regarding each method/approach used for hydrate calculations. In addition, choosing an accurate prediction tool that may serve as an optimization tool is also of vital importance. The selected approach should be able to predict as accurately as possible hydrate formation at specific temperature/pressure, at a given overall composition. By providing such a tool, the oil and gas industry will be able to decrease the daily operation expenditure (OPEX) by decreasing the inhibitor cost. An accurate trustful hydrate predicting approach may serve as an optimization tool for inhibitor volume/cost. This is accomplished by minimizing the required shifting of hydrate formation conditions (P-T) toward higher ones, at which more energy is required in the system to form hydrate. To achieve that, the used approach/tool must be able to predict accurately the inhibition effect. By attaining this goal, we help in optimizing and identifying the best method needed to be applied in pipelines to avoid blockage. Such a tool provides necessary information about different inhibitors scenario (type and concentration) and other methods (e.g. Cold flow) that can be applied to avoid pipeline blockages. By doing so, the oil and gas industry will be able to compare accurately different methods based on while low financial cost, efficiency, and validity will be accomplished together for different cases.

Based on that, in this work, we considered the six well-known approaches that have been recommended and reported as of today's most accurate and state-of-the-art ones for hydrates modeling. These approaches are implemented in four commercial software packages considered as today's best solutions offered in the market for modeling hydrates. However, this study can be considered as a state-of-art for the hydrate prediction accuracy of the already market's present programs. A comparison is provided based on hydrate formation pressure/temperature. All of these methods/approaches are tested against a large number of experimental hydrate pressure and temperature dissociation data collected from the literature, published between the years of 2015 and 2020. In this chapter, only data related to systems containing CO₂ are discussed and results obtained are analyzed both quantitatively and qualitatively.

6.2 Background of the Study

The background of this study is mainly related to oil and gas transportation in pipelines. Thus, accurate predictions of natural gas hydrates formation and inhibition effect is of main interest. To examine the accuracy and prediction strength of each approach, experimental data are reproduced within each approach. Within specific methodology, the deviations of each method are examined. Consequently, analysis and recommendations based on the results obtained are reported. To investigate the accuracy of different models, present, several factors have been taken into consideration. The most important factor is the presence of CO₂ components in the system and inaccuracy introduced due to its non-ideal behavior.

Thus, the CO₂ component is a good start to test the strength and accuracy of each approach used.

6.2.1 The Need of an Accurate Model for CO₂ Hydrate

Several organizations and environmental committees (e.g. European Projects Association (EPA)) are focusing on reducing CO₂ emission from large power plants and major industrial processes by capturing the CO₂ for geological sequestration. Several reports have investigated the potential for geological sequestration of CO₂ and association costs related to the outcome of which is that CO₂ storage in Deep Ocean is the likely long-term destination of the large atmospheric releases of CO₂ in Europe. Under the conditions prevailing at Deep Ocean (low temperature, high pressure) and the contact of CO₂ with seawater, CO₂ hydrates are formed. The necessity and the low cost of CO₂ storage in Deep Ocean encouraged different institutes and industries to run dozens of projects on the application of this method for reducing CO₂ concentration in the atmosphere. However, crucial factors that are considered in the application of this method are the formation and stability of CO₂ hydrates in the Deep Ocean. An accurate prediction of these factors requires a capable and accurate hydrate approach/model. As a result, the outcome of CO₂ hydrate modeling in this work can be adopted as a clustering tool for the accuracy of different approaches studied in. Besides, the recommended approach can be used directly for studying the above-mentioned factors.

6.3 Theory and Approaches

The approaches used in this study are today's best methods predicting hydrates dissociation conditions of a given overall composition. These methods may be classified based on similarities or differences in which several thermodynamic models are used. All of these approaches use the van der Waals-Platteeuw model together with a Kihara spherical core potential. Most of them implement VdW-P in an explicit fugacity-based method for calculating gas hydrate equilibrium conditions. Only one out of six approaches studied uses water chemical potential difference between empty and actual hydrate for computing equilibrium conditions. However, they differ in the thermodynamic and EoS models describing the hydrate co-existent phases (e.g. ice, water, etc.). All that has been mentioned is explained in detail in both chapters 4 & 5. Chapter 4 covers the original VdW-P model, it is a modification and different way of implying this model for hydrate equilibria problem. Chapter 5 covers different thermodynamic and EoS models used for the description of hydrate co-existing phases. In this section, we will review each approach Models used to describe equilibrium in all phases of a hydrating system.

6.3.1 Approach N°1: Parrish and Prausnitz (1972) "CSMHyd"

(Prausnitz W 1972) Were the first who presented an algorithm for VdW-P theory to become suitable for computer implementation. The first program that adopted and implemented this model is the CSMHyd program (Sloan ED 2008). Sloan has shown that the P-P model can similarly be derived by the use of statistical mechanics. However, P-P derived their model by use of a chemical reaction theory and classical thermodynamic relations basis (Section 4.3). Despite that, CSMHyd adopted the P-P method in which the main feature used in this study is hydrate temperature or pressure predictions.

The basis of the model present in CSMHyd assumes that within the presence of the four factors, i.e. water, light hydrocarbon gases, low temperature and high pressure, hydrate is always formed. In other words, no stability analysis targeting different combinations for phase fractions/compositions that minimize locally or globally Gibbs energy and satisfy material balance is needed. Accordingly, the predicted hydrate's structure (sI and sII) are based on an already introduced instruction to the algorithm. For example, CO₂ pure hydrate always and only forms an sI structure. On the other hand, the model/program identifies the formation of hydrate within the ice/water co-existing phase based on a reference temperature of 273.15 K which denotes the triple point of water. Accordingly, if $T < 273.15$ the model assumes ice presence whereas water is assumed if it is equal or higher. Similarly, the model identifies the vapor or condensed gas region (different locus of P-T diagram) based on quadruple experimental data points collected from the literature for different gases. Regarding CO₂ the upper quadruple point conditions for hydrate of pure CO₂ gas are 283.5 K and 4.537110 MPa. The model adopts these values and will check for the T of the system. If $T < 283.5$ it assumes that pure CO₂ hydrates form in the region of hydrate-water-vapor region. If not, hydrates will form in the water-condensed gas region at higher pressure.

On the other hand, the chemical potential difference between empty and actual hydrate is used for the calculation of equilibrium conditions. It aims at the basis that chemical potential is a state function and by equalizing theoretical to experimental difference and iterating for the pressure, dissociation/formation pressure of hydrates is calculated. A typical Newton-Raphson technique is used for this purpose. For full detail of the algorithm and steps followed review section 4.3. Finally, the Soave-Redlich-Kwong equation is used to model hydrocarbon phases in the model. However, the fugacity of water and gas dissolved in the aqueous phase are treated using fundamental thermodynamic relationships explained in section 5.4 of this work.

6.3.2 Approach N°2: Ballard and Sloan (2002) “CSMGem”

After the adoption of the Parrish and Prausnitz method in CSMHyd software developed by E. Sloan, the main improvements on the hydrate phase equilibria problem occurred. It made it provide a faster and safer prediction of the hydrate equilibrium conditions. The new method allows direct calculation of water fugacity in hydrate instead of equalizing the chemical potential difference. Moreover, it provides a faster convergence to the solution by eliminating the second iteration required by the P-P method. While that improvement happened, Ballard was running spectroscopic experiments for his Ph.D. under the supervision of Prof. Sloan. During the evaluation of the spectroscopic data obtained, they realized significant deviations between VdW predicted values and the experimental data obtained. Based on that, they proposed modifications to the original hydrate theory of VdW-P. The main modification aims at adding an activity coefficient to the original theory to account for the distortion of the lattice structure by guest molecules. The second modification provided an easier way for the calculation of water fugacity in hydrates that made it easy to describe in a thermodynamic sense. On the other hand, several two-phase stability and phase split tests/approaches were extended to include multiphase systems, such as Gupta's and Michelsen's approaches. After all these improvements that may provide more accurate and reliable results,

Sloan's added these auxiliary tools for approach N#1 adopted in CSMHyd. He came up with a new approach (N#2) and implemented it in another software "CSMGem", an acronym for Colorado School of Mines (Gibbs energy minimization).

This approach (Approach N#2) utilizes the same models already used in Approach N#1 (CSMHyd) for describing different hydrate co-existence phase. It also uses Soave-Redlich-Kwong (SRK) EoS for modeling different hydrocarbon phase but also treats gas dissolved and water in the aqueous phase using classical thermodynamic relationships (Section 5.4). The two modifications of Ballard to the original VdW-P hydrates model are explained in Chapter 4. Also, Gupta's stability analysis for phase existence/absence implemented in this approach is explained in Chapter 2. It is good to mention here that to initialize or to start the algorithm described in Chapter 2 by mean of K_i 's, Sloan has reported/used two sets of K_i 's. Both sets can be used as an initial guess. The first set is generated using composition independent correlation "ideal set K_i 's" while the second one is based on incipient solid phases. CSMGem gives the choice to identify one of these sets to start calculations. Although K_i 's don't play an important role in the solution and are just used as an initial guess for the algorithm, in this work we choose the ideal set of K_i 's to start our calculation. The reason for that is to ensure that both methods/approaches (N'1 & 2) do have the same basis in the computation procedure. Since no data is available about the initial guess used in CSMHyd (N#1) approach and by taking into consideration the year of implementing Parrish and Prausnitz method into CSMHyd program (1998) were few experimental data on solid phases was available, we have assumed that Sloan's has been using the same ideal K_i 's in his previous approach (N'1).

It is also important to mention that based on the fact that Gupta's stability method is present in this approach, no more quadruples data point entry is needed in the algorithm. The outcome of Gupta's stability method visualizes the presence or the absence of each phase assumed (Chapter 2). In other words, the presence of a vapor or condensed gas phase is based on the outcome of Gupta's stability parameter. However, the same idea is applicable for the aqueous phase, where it is not anymore defined by a temperature condition but also depends on Gupta's test outcome parameter.

6.3.3 Approach N#3: KBC/MultiFlash RKSA "MF RKSA"

MultiFlash/KBC RKSA's first two words refer to industrial names of the software (MultiFlash) and the company name providing this approach (KBC). RKSA is an acronym in which the first three letters refer to SRK/RKS EoS used in the model and letter A to the advancement made. All together form Redlich-Kwong-Soave-Advanced. However, the major improvement in this model/approach is the presence of an improved NRTL (Non-Random-Two-Liquids) equation. This allows the complex behavior of the liquid phase to be represented, whilst maintaining the good performance of cubic EoS for hydrocarbon phases.

In this work, we will be referring to the approach (N#3) by the abbreviation "MF RKSA". In this model, the calculation of hydrates phase equilibria is based on the improved Parrish and Prausnitz method. Through an "improved" explicit fugacity-based method for calculating gas hydrate equilibrium conditions is denoted. It becomes clear now, that the solved equation is the equality of component's fugacity in all phases present at equilibrium. As it is the case in CSMGem and the

presence of Gupta's application that ensures the stability of phases at equilibrium, the Michelsen multiphase stability test is used in this MF RKSA. Both methods are used for checking the stability of possibly existing phases. However, the procedure followed in each one varies. In MF RKSA, Michelsen's stability main objective aims at finding phase compositions at which the Tangent Plan Distance (TPD) is negative. However, material balance is respected in the test by definition (by assuming an infinitesimal quantity of the trial phase). Based on that, the phase presence is identified by the Michelsen test where no preliminary conditions are used.

On the other hand, gas and liquid hydrocarbons phases are modeled with the SRK EoS model. However, the fugacity of liquid hydrocarbon is described by the generalized equation explained in section 5.2. The first term in the equation is the activity coefficient. As it is explained in section 5.3 it accounts for Excess Gibbs energy. While explaining Eq.5. 29 in Chapter 5, the case has been considered is that only the EoS equation is used for the description of the liquid phase. Due to that, the activity coefficient has been neglected. However, in this approach, both the EoS and activity coefficient is used to represent the liquid phase. In other words, the activity coefficient is activated for any liquid phase present in the system. In general, the activity coefficient is used to model liquid phases containing any combination of polar and non-polar components exhibiting a very strong non-ideality. However, it can be obtained using various equations such as Wilson, UNIQUAC or NRTL. In this approach (MF RKSA), the NRTL equation is adopted for this purpose. NRTL discussion is not present in this work since it is out of the scope, for more details refer to any thermodynamic textbook. Additionally, other factors in Eq.5. 29 account for the correction of fugacity through Poynting correction. All terms present Eq.5. 29 exception of the activity term can be combined to form Eq. 5. 30. This equation is just a combination of the fugacity coefficient of components obtained from SRK EoS and the saturation pressure of the component. Adding to that, the Poynting correction term is present.

Apart from the gas and liquid phases, the aqueous phase is also calculated using Eq.5. 2 in the same way, described before. In general, the activity coefficient will be always activated for the aqueous phase.

However, no big effect is observed in the results when pure water is present. This term becomes important when CO₂ is dissolved in water.

The only remaining phase that needs to be modeled is the solid phase. Utilizing solid phase, solid CO₂ and ice are referred. To represent the solid phase, MF-RKSA uses the Solid Freeze-Out model described in 5.3.3.

6.3.4 Approach N#4: KBC/MultiFlash CPA "MF CPA"

Due to the difficulties present in modeling the aqueous phase, particularly if inhibitors and/or salts are present, MultiFlash software provides an alternative model/tool for modeling hydrates. However, KBC/MultiFlash Company recommends the use of this model/approach for systems including inhibitors. This approach is based on the CPA EoS to represent all phases present in a hydrated

system. Based on that, the CPA EoS represents each phase having both non-association and association terms. Dealing with vapor hydrocarbons, the non-association term is always present and represented by the SRK cubic term. On the other hand, the association term is only activated when polar components such as CO₂ exists in the gas phase. CPA also covers the liquid hydrocarbon phase in the same way. For an aqueous phase and for both cases of water with/without dissolved gas (e.g. CO₂ or methane), both terms of the CPA are always present. The reason is that water is a polar compound, thus hydrogen bonding needs to be represented within the second term. For a solid phase, this approach adopts the Solid Freezeout model presented in section 5.3.3. The basis of which different energy terms should be included. Finally, MultiFlash software adopts Michelsen's test for phase stability in different hydrate approaches supported.

6.3.5 Approach N°5&6: HydraFLASH/HydraFact CPA, Both Approaches “HF” & “HF72”

Hydra Flash/Hydra Fact is the names of the software and the developing company providing it respectively. In this software, a CPA-EoS based model is used to perform hydrate calculations. However, due to the difficulties in representing hydrate-co existence phases, HydraFLASH software gives the user the choice to select the cubic part of the CPA EoS. Based on that two non-association-cubic EoS are used to describe each system of this work. The first chosen EoS is Soave-Redlich-Kwong while the second one is SRK72. Since both approaches are CPA based ones with differences in the association term, they are labeled as HF & HF72. In both approaches, the CPA EoS covers all phases present in a hydrated system. However, the association term is activated only when polar components are encountered in some phases. On the other hand, in both approaches, HF & HF72, the solid phase fugacity is corrected using the Poynting method described in 5.3.2. Finally, the already described Michelsen's multiphase test is used to ensure the stability of all phases in equilibrium.

6.4 Experimental Work

6.4.1 Methodology

All experimental data are available in the literature that was published after 2015 and were retrieved and organized according to their content (i.e. CO₂ mixtures, salts, inhibitors, etc.). In this Chapter, only data related to systems containing CO₂ are discussed. Subsequently, all data were introduced to the software available, namely Hydra Flash (Hydra Fact), MultiFlash (KBC), CSMGem (Colorado School of Mines) and CSMHyd (also Colorado School of Mines). All experimental data related to CO₂ mixtures were reproduced using different approaches/models present in every software:

- HydraFlash with SRK non-associating term (HF).
- HydraFlash with SRK72 non-associating term (HF72).
- Multiphase Flash with CPA model (CPA).
- Multiphase Flash with RKSA model (RKSA).
- CSMGem.

- CSMHyd.

After that Excel files were generated including all results obtained from the software packages. As CSMGem and CSMHyd approaches did not converge for a significant number of cases, HF, HF72, MF RKSA, and MF CPA approaches were firstly compared separately. Subsequently, all six approaches were compared only for the cases where convergence was achieved by all packages. Distinguishing between convergent and non-convergent data points allows for a fair comparison between different approaches.

6.4.2 Error Indices

The experimental data structure in all Excel sheets was based on the data Paper index number, Sample number (experiment set in every paper) and Number of experiment points regarding the sample/experimental set number in every paper. After that, both experimental measurements and predicted values are presently followed by the accuracy of each approach which was obtained by computing various error indices. The defined Error indices used for this purpose are:

- Absolute Error (AE) that is predicted vs. Experiment data
- Absolute Relative Error (ARE) defined as $\text{Absolute Error} / \text{Experiment Value}$
- Cumulative Average Absolute Relative Error (CAARE) that is the Cumulative average of the Absolute Relative Error (starting from the experimental point exhibiting minimum T or P)
- Cumulative Absolute Relative Error (CARE) that is the cumulative sum of the Absolute Relative Error
- Cumulative Average Absolute Error (CAAE) that is the cumulative average of the Absolute Error starting from the experimental point exhibiting minimum T or P
- Cumulative Absolute Error (CAE) that is the sum of the Absolute Error.

6.5 Results and Discussion

After computing all error indices, the data points were arranged in increasing order of Pressure or Temperature. For data visualization, two series of plots were generated illustrating the relative Error and the absolute Error, labeled as A and B respectively. Series A, B includes two categories as following:

1. **A1 series:** Error Indices vs (T or P) for interval of industrial interest (T low/Plow) for HF, HF72, MF (CPA) and MF (RKSA).
2. **A2 series:** Error Indices vs (T or P) for interval of transport and desalination interest (T high/P high) for HF, HF72, MF (CPA) and MF (RKSA).
3. **B1 series:** Error Indices vs (T or P) for interval of industrial interest (T low/Plow) for HF, HF72, MF (CPA) and MF (RKSA) , CSMGem and CSMHyd.
4. **B2 series:** Error Indices vs (T or P) for interval of transport and desalination interest (T high/P high) for HF, HF72, MF (CPA) , MF (RKSA) ,CSMGem and CSMHyd.

6.5.1 Effect of Temperature (HF, HF72, MF(CPA) And MF (RKSA))

6.5.1.1 A1 Series (Low Temperature [273-283 K])

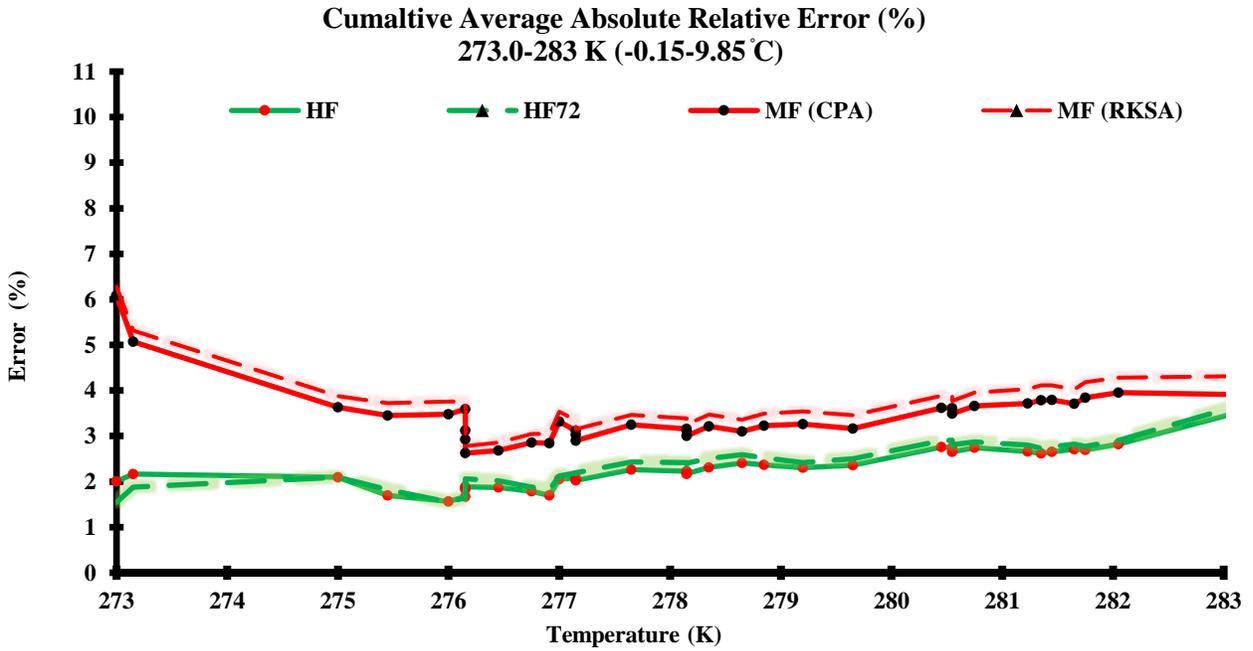


Figure 20 Cumulative Average Absolute Relative Error (%) vs. temperature (K) [273.0-283 K]

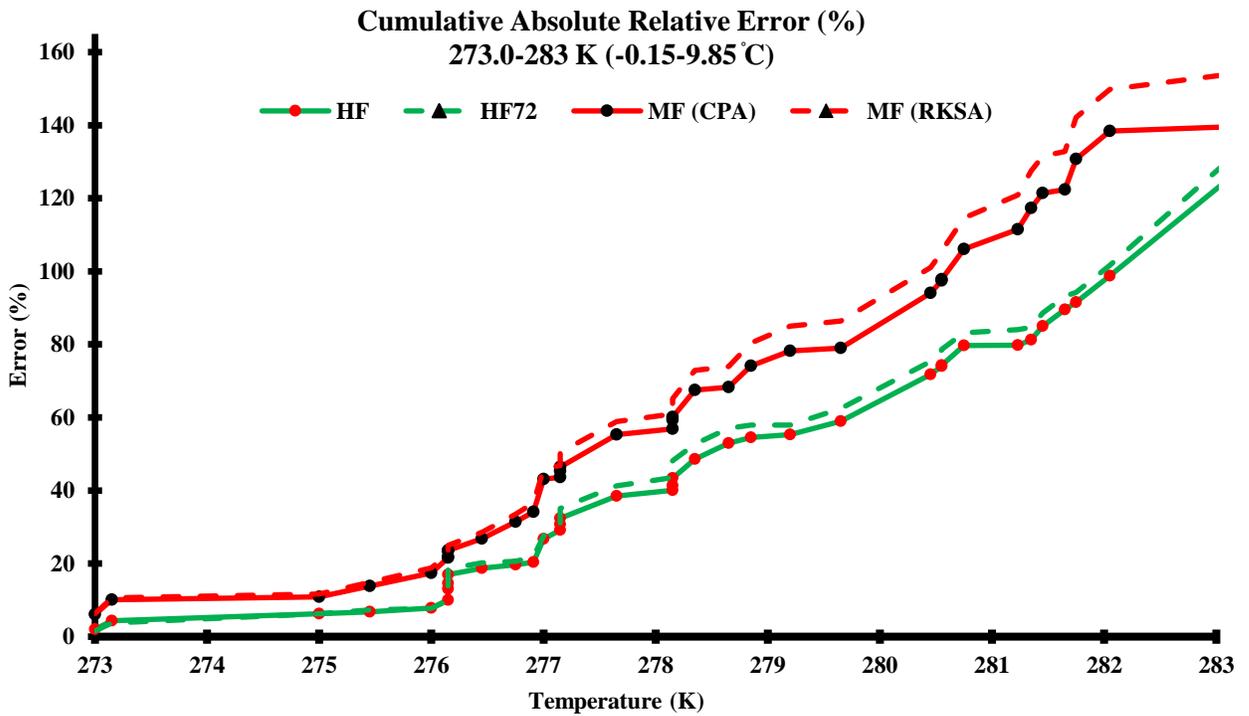


Figure 21 Cumulative Absolute Relative Error (%) vs temperature (K) [273.0-283 K]

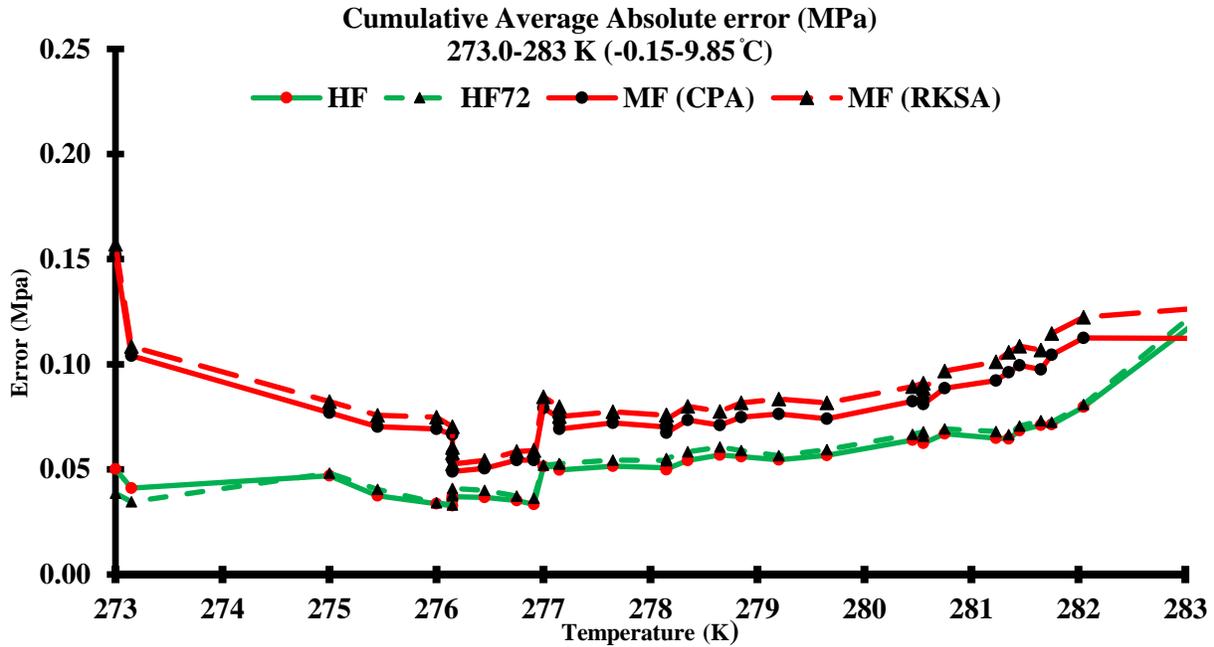


Figure 22 Cumulative Average Absolute Error (MPa) vs. temperature (K) [273.0-283 K]

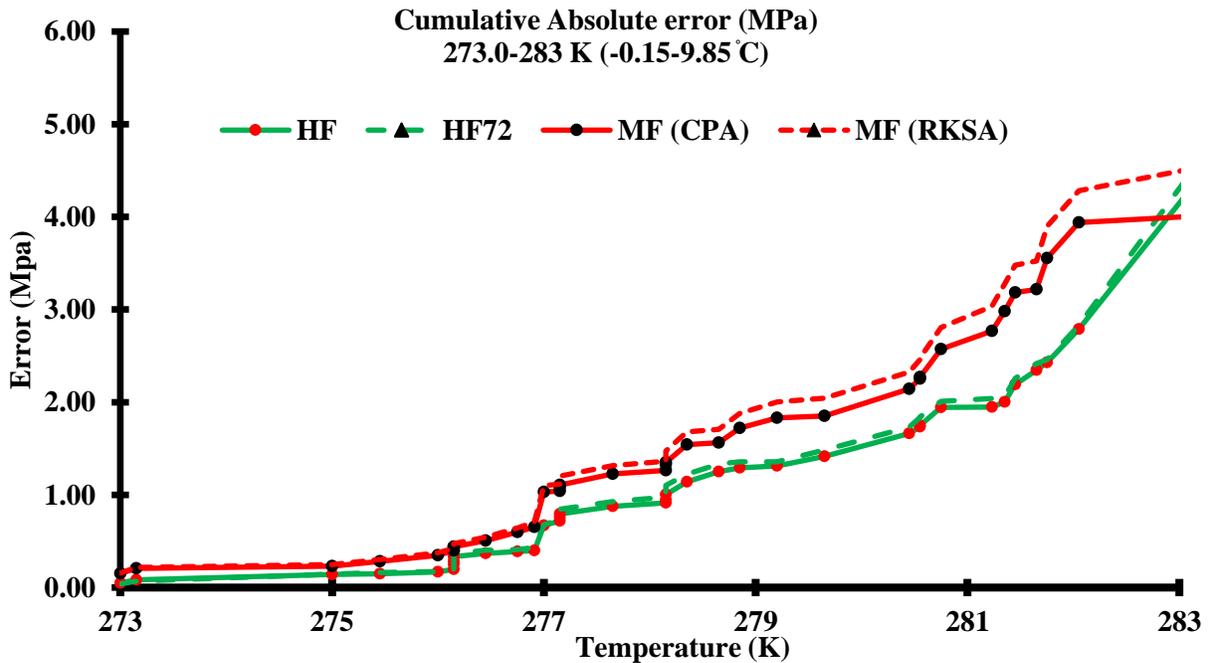


Figure 23 Cumulative Absolute Error (MPa) vs temperature (K) [273-283 K]

Figures 20, 21, 22 and 23 show different error indices for low temperature range (273-283 K). Examining the results obtained for low-temperature range (273-283 K) present in series of figures, a clear difference in the accuracy/deviation between MultiFlash and HydraFlash approaches adopted is noticed. Also, it is quite clear that approaches adopted by each software show more or less the same deviation at low temperatures. While reproducing the data related to this part (low

T), both software approaches predicted the same equilibrium phases, but also the same hydrate structure (sI). Thus, Michelsen tests present in both software (MF, HF) has converged similarly. Consequently, a general conclusion for this part can be made that MF RKSA/ MF CPA and HF/HF72 approaches exhibit similar capability of representing equilibrium phases in a low-temperature range. Focusing now on HydraFlash approaches HF & HF72, despite the difference in the non-association term of CPA present, both approaches show a similar deviation at the low-temperature range. Thus, it can be said that both EoS (SRK-SRK72) that covers the non-association term in the CPA model makes no difference at a low-temperature range in the CO₂ systems studied.

On the other hand, knowing that MF RKSA and MF CPA represent equilibrium phases using activity and CPA based models respectively, both approaches show almost the same accuracy at low temperature. Thus, it can be said that MF RKSA or activity coefficient model has no more or fewer advantages on the CPA EoS model at the low-temperature range. The fact that both models present in MultiFlash software show this behavior at low T is explained as following: at low temperature and pressure, phases (mainly gas at low T) do have an ideal behavior, which means it is easier (regarding other T & P conditions) to be represented by both methods (MF RKSA/MF CPA). The accuracy effect here is not related to the model itself rather than the parameters used in each one of them. Within the results, it could be said that certainly HF & HF72 predicts more accurately than both MF RKSA and MF CPA approaches for low temperature range.

6.5.1.2 A2 Series (High Temperature [283-295 K])

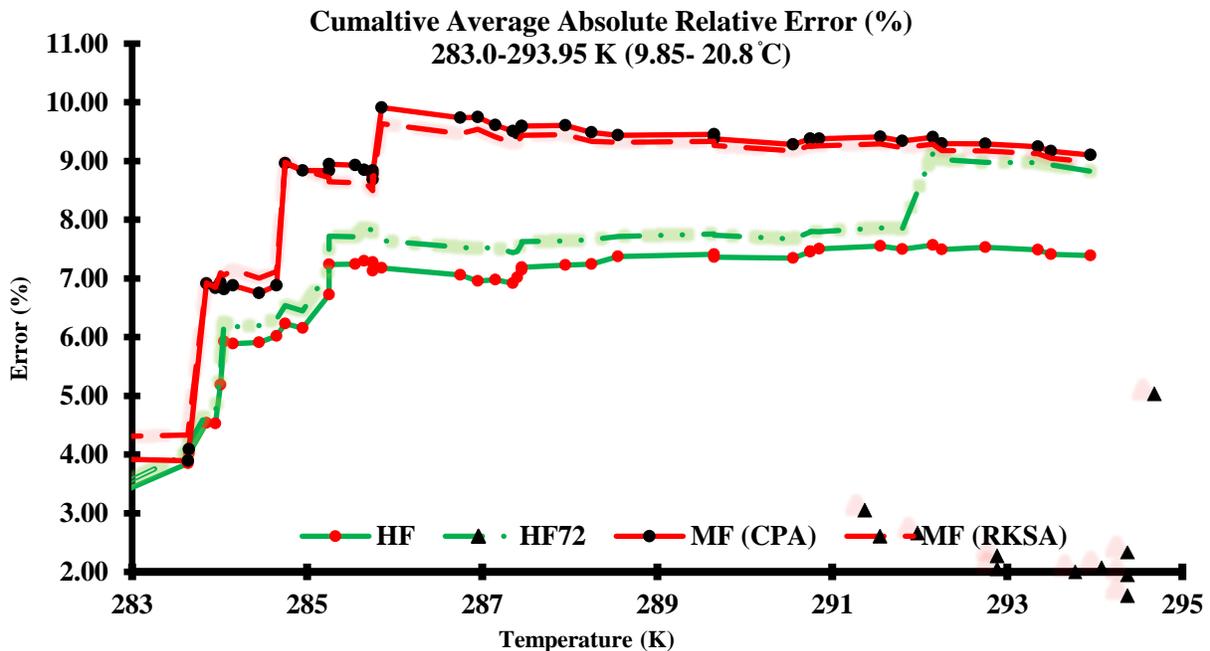


Figure 24 Cumulative Average Absolute Relative Error (%) vs. temperature (K) [283-293.95 K]

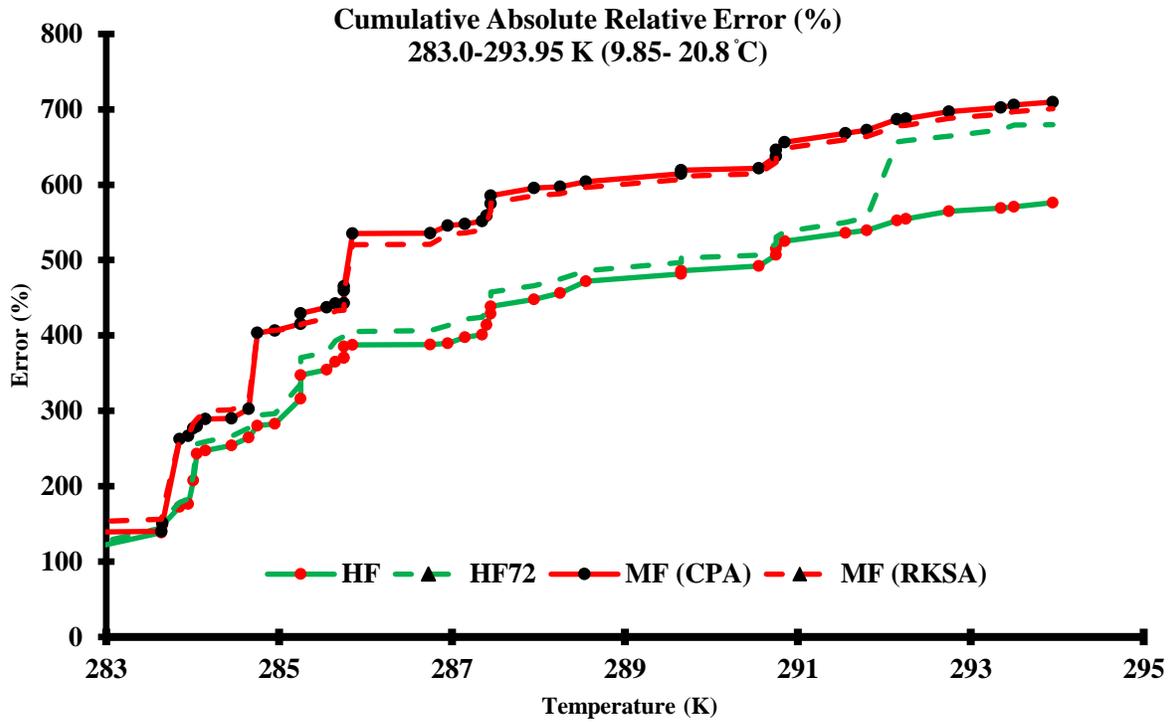


Figure 25 Cumulative Absolute Relative Error (%) vs temperature (K) [283.0-293.95 K]

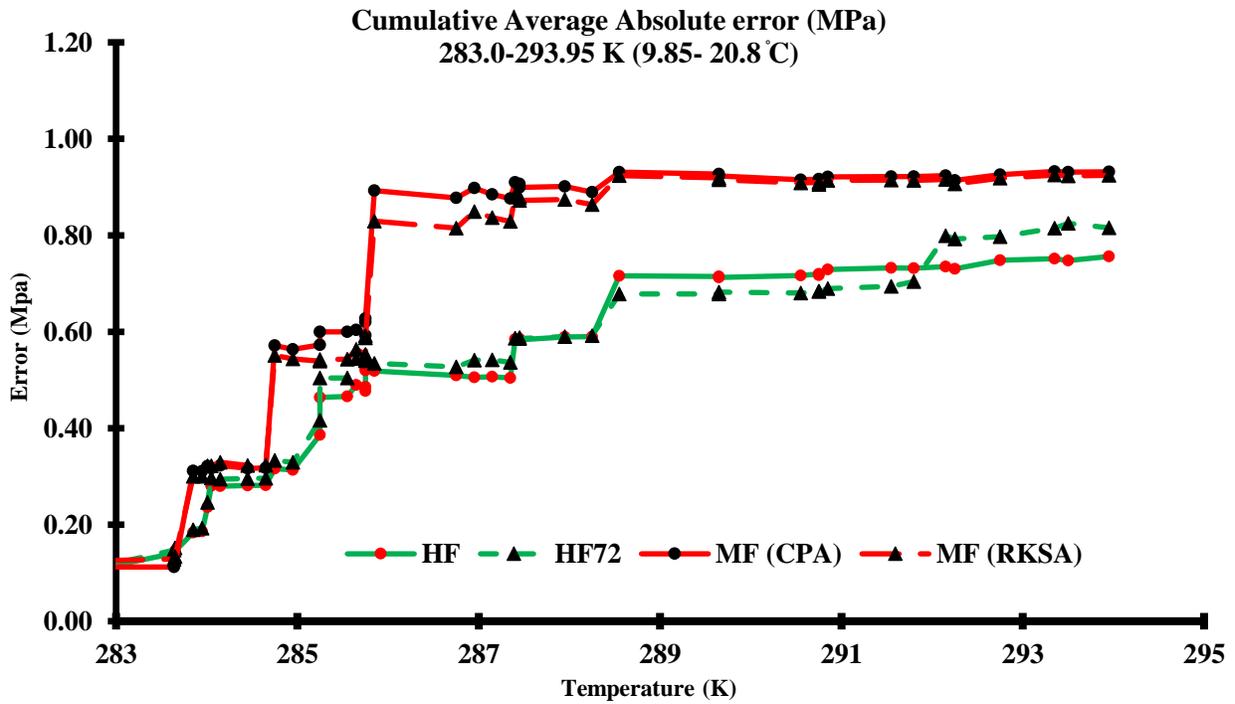


Figure 26 Cumulative Average Absolute Error (MPa) vs. temperature (K) [283.0-293.95 K]

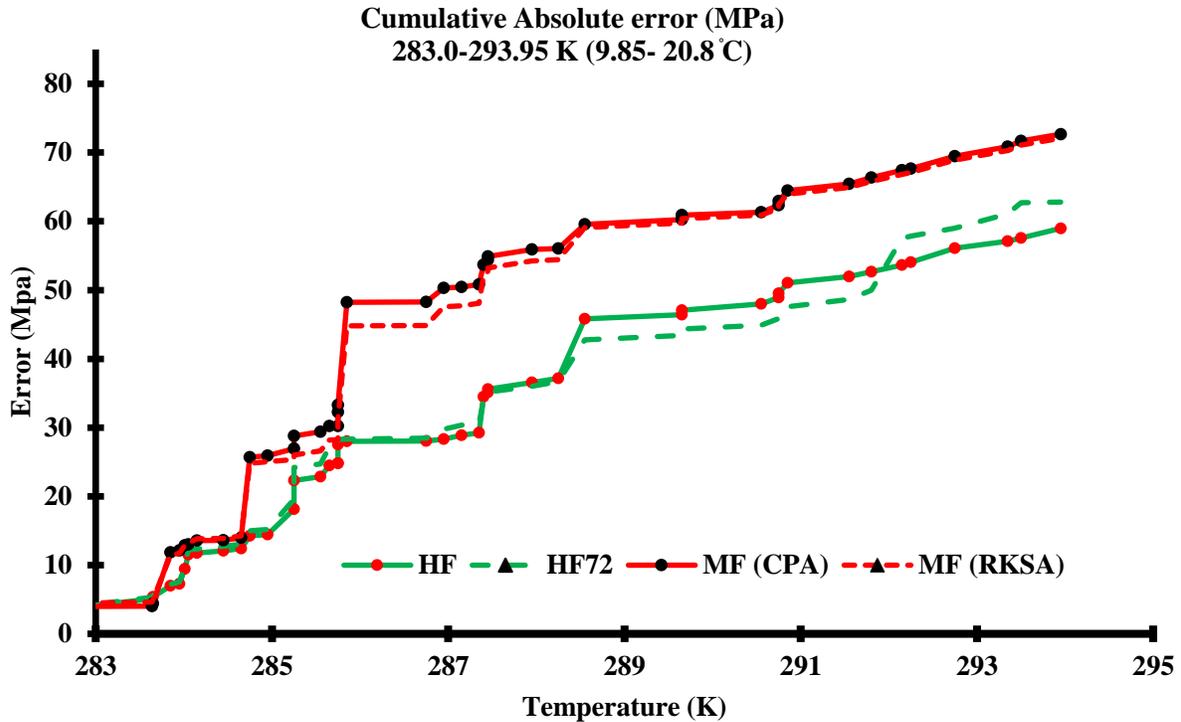


Figure 27 Cumulative Absolute Error (MPa) vs temperature (K) [283-293.95 K]

Figures 24, 25, 26 and 27 show different error indices for high temperature range (283-295 K). In the series of figures, it is noticed that as temperature increases between values of 283 and 286 K, the slope of deviation exhibited by both MF RKSA & MF CPA approaches is significantly higher than the ones of both HF & HF72 approaches. However, the increase in the deviation of all approaches between 283 & 286 K is mainly due to phase transition. After phase transition, a plateau behavior appeared, thus it is due to the stable structure predicted in all approaches.

It is obvious that HF & HF72 approaches exhibit higher accuracy (low deviation) than the other two approaches of MultiFlash software present (MF RKSA and MF CPA). Within the results and results obtained for low-temperature range for HF/HF72 at low temperature, it could be said that certainly HF & HF72 predicts more accurately than both MF RKSA and MF CPA approaches for whole temperature range.

To explain HydraFLASH approaches accuracies showed in figures mentioned above (Low temperature/High temperature), HF & MF CPA are compared to each other. The reason for choosing these two approaches and not others is explained by the fact that both approaches represent the same basic model (CPA EoS). Consequently, a better understanding of HF accuracy will be present.

Firstly, the non-association term which is represented by a cubic EoS can be eliminated from our comparison for two reasons. The first one is that in both approaches (MF CPA, HF), the EoS type used is SRK. The second reason is the results already obtained in the first part of the discussion,

stating that no effect of the EoS type on the accuracy of any CPA model covering CO₂ systems at the low-temperature range. Thus, only the non-associated part of CPA should be considered. Referring to the mentioned part of the equation, the difference that could be present between HF & MF CPA is association parameters (σ , ε/k) included in the association (binding) strength term of the CPA equation. These parameters are fitted to equilibrium data. Thus, it can be said that association parameters are more accurately tuned/fitted in HydraFlash rather than MultiFlash for the low-temperature range.

6.5.2 Effect of Temperature (HF, HF72, MF(CPA), MF (RKSA) ,Csmgem And Csmhyd)

6.5.2.1 B1 Series (Low Temperature [273-283 K])

As CSMGem and CSMHyd approaches did not converge for a significant number of cases, HF, HF72, MF RKSA, and MF CPA approaches were firstly compared separately. Considering the non-convergence of CSMHyd, it can be referred to as the lack of stability within the algorithm. On the other hand, the non-convergence of CSMGem Based can be argued that numerical failure is present in the algorithm for which both stability/M.B and thermodynamic should be satisfied simultaneously.

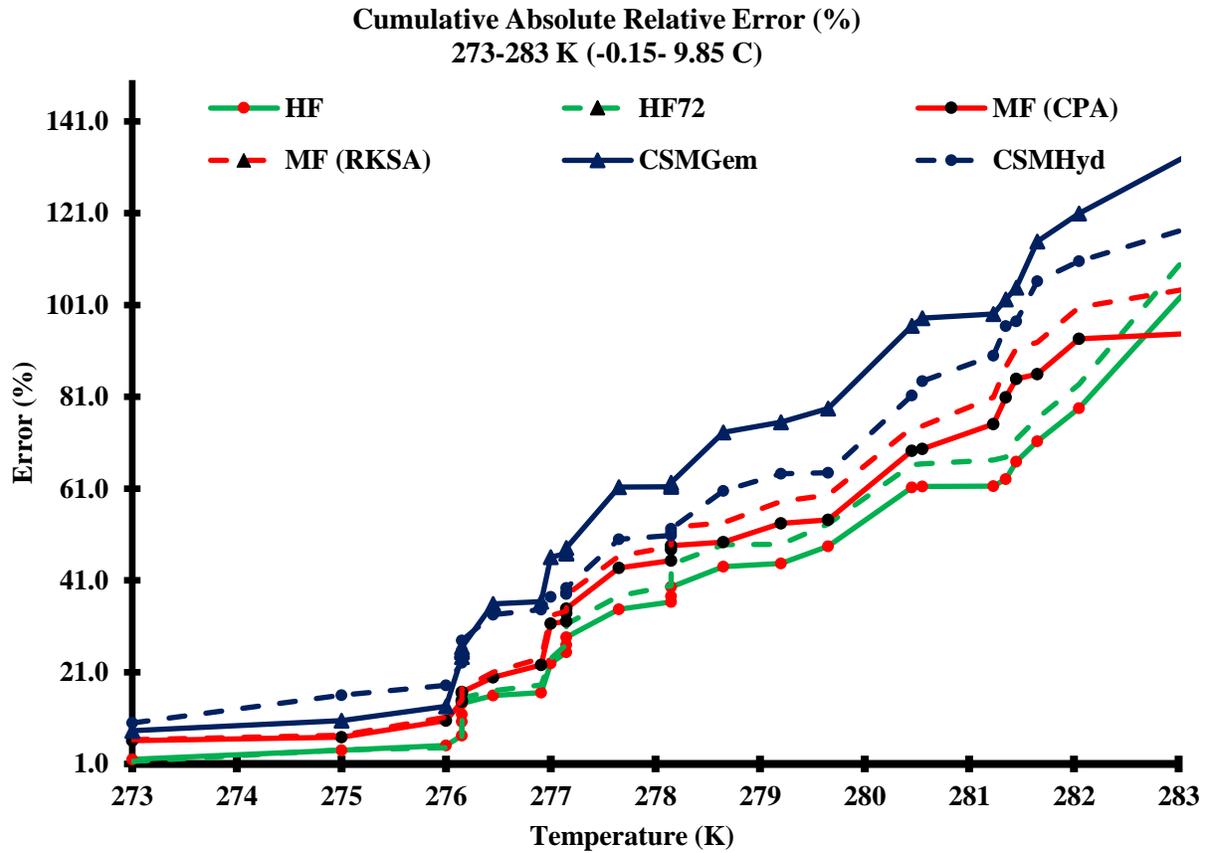


Figure 28 Cumulative Absolute Relative Error (%) vs temperature (K) [273.0-283 K]

By considering only the systems that have converged for all six approaches, other series of figures (B1 6.5.2.1) then are generated. Examining the results of the low-temperature range (figures 28 and 29), it is demonstrated that all approaches show a monotonic increase. It is also clear that HF & HF72 still exhibiting the lowest deviations/higher accuracy among all other approaches (MF CPA, MF RKSA, CSMGem, and CSMHyd).

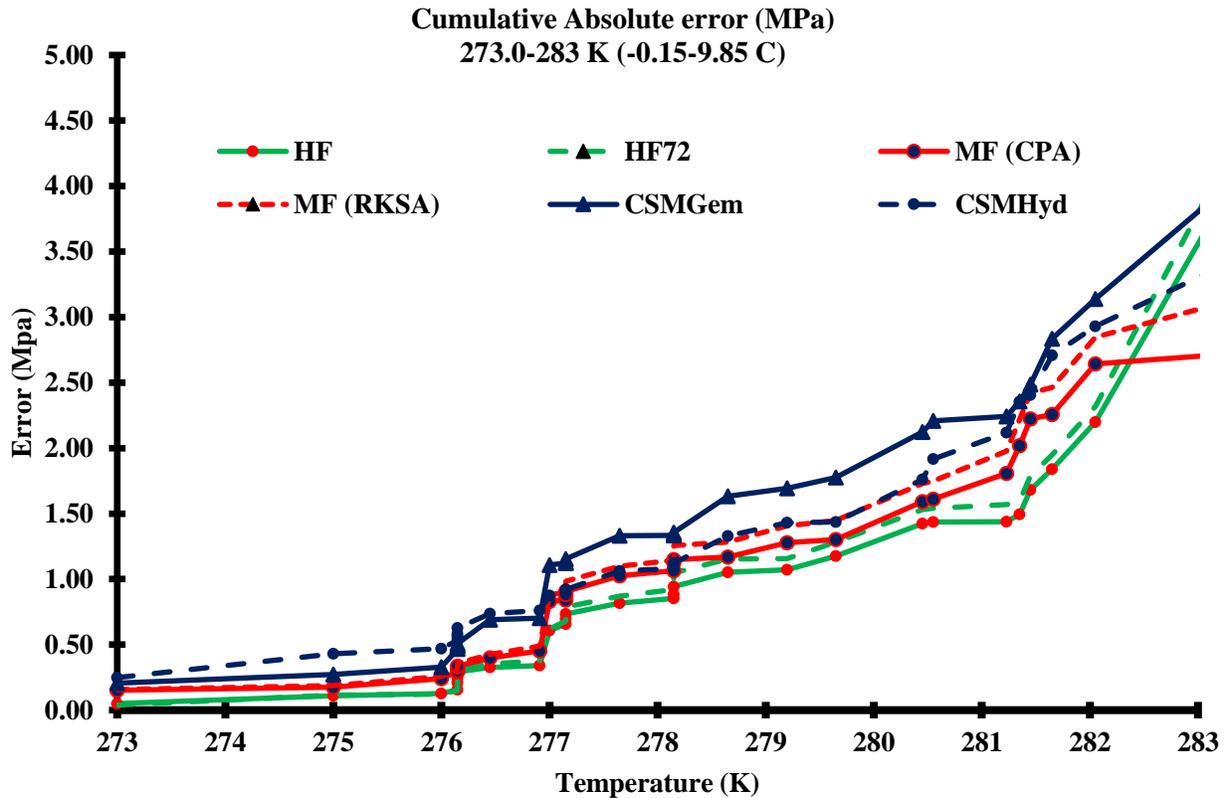


Figure 29 Cumulative Absolute Error (MPa) vs temperature (K) [273-283 K]

In both figures 28 and 29, CSMGem shows the highest deviation between all approaches presented. To explain CSMGem inaccuracies (Low temperature/Six approaches), CSMGem & CSMHyd are compared. Reasons for choosing these two approaches and not others are explained by the following points:

- All approaches and stability tests predicted same equilibrium phases (No stability problem)
- Both CSMHyd and CSMGem represent equilibrium phases in a thermodynamic sense.

Based on that, by focusing on the differences of both approaches (CSMGem & CSMHyd) causes of the inaccuracy can be found. CSMGem differs from CSMHyd within the hydrate model in which the first one adopts modifications of Ballard (2002) while CSMHyd adopts the original model of vdW-P. the other difference present is also Kihara's parameters difference between both models. Both reasons can play a major role in the accuracy of CSMGem approach.

6.5.2.1 B2 Series (High Temperature [283-293.95 K])

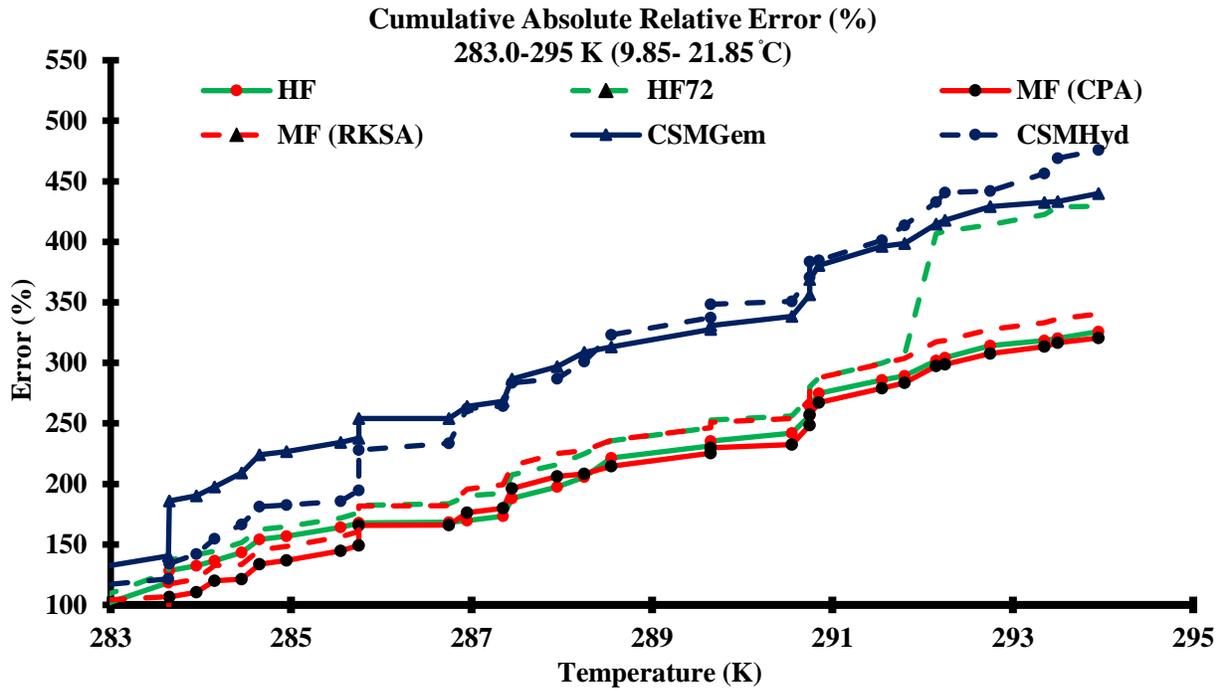


Figure 30 Cumulative Absolute Relative Error (%) vs temperature (K) [283.0-293.95 K]

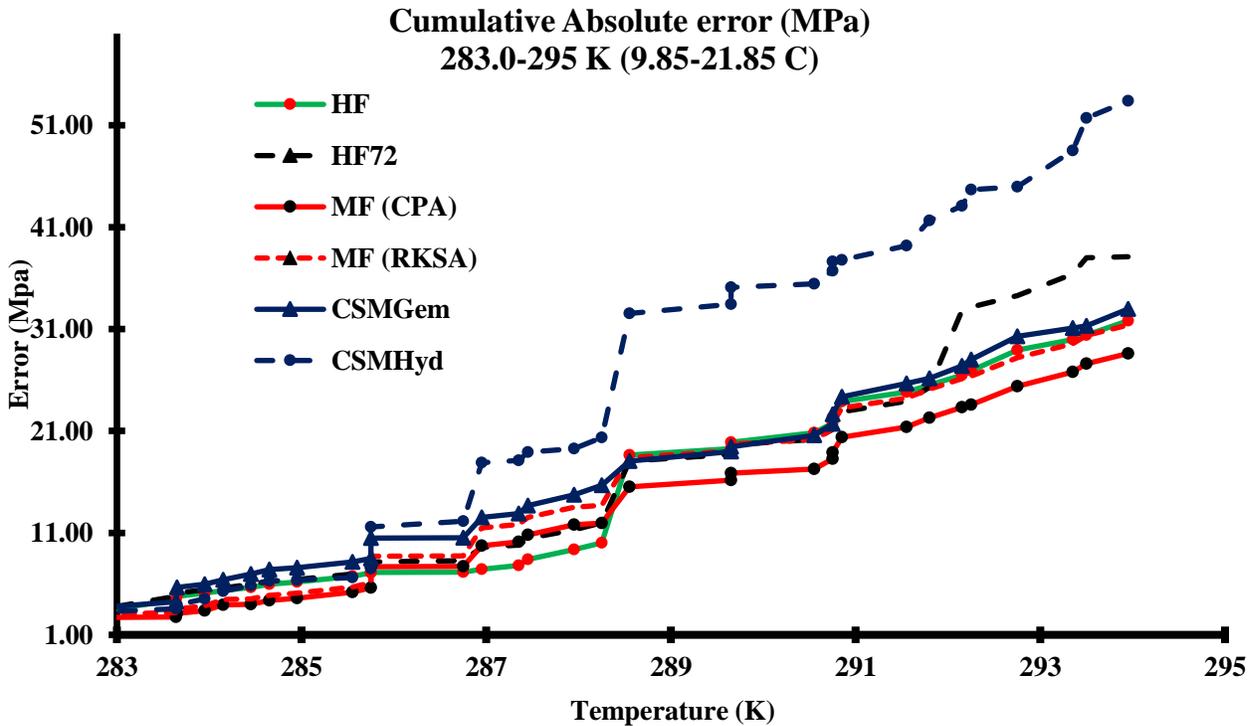


Figure 29 Cumulative Absolute Error (MPa) vs temperature (K) [283-293.95 K]

Previewing high-temperature results (figures 30 & 36), it is clear that the highest deviation is referred to CSMHyd approach. Which exhibits a significant deviation of 51 MPa (Cumulative Absolute Error) at the highest temperature. This deviation or inaccuracy is due to lack of stability test in CSMHyd approach for which it predicts sI hydrate at equilibrium while other approaches predicted sII. Thus, the CSMHyd approach is not providing stable results. Looking at all error indices figures it could be said that CSMGem performs far superior to CSMHyd, but still exhibiting the lowest accuracy among all other approaches used in this study.

6.7 Conclusion

The following conclusions can be drawn from the experimental results obtained in this study:

- HF72 and HF approach (HydraFLASH) and MF RKSA & MF CPA Multiphase Flash perform far superior to CSMHyd and CSMGem approaches present in both Sloan's software as the latter was not even able to provide predictions for some of the cases examined.
- The non-convergent systems within CSMHyd approach/Software are explained by the lack of stability, where no stability test is present in the algorithm for which gas/condensed hydrocarbon region identification, as well as ice/water presence, are based solely on already implemented conditions (quadruple points for pure gas hydrate system, triple point of pure water 273.15K)
- Although CSMGem checks for stability using Gupta's approach and all convergent systems identified the same phase present at equilibrium as the ones in MultiFlash and HydraFlash, the only reason that can be attributed for the lack of convergence is a numerical failure. This problem is frequently present when an additional parameter (Guptas' stability parameter) is included in the original problem.
- Although CSMGem adopts the modified Van der Waals-Platteeuw theory suggested developed by (A.L Ballard 2002) accounting for distortion of the lattice structure, it still exhibits the highest deviation/error compared to MultiFlash and HydraFlash approaches. This can be explained by the fact that CSMGem treats all phases in a classic thermodynamic sense while others (HF, HF72, MF CPA, and MF RKSA) use advanced models to account for inter/intramolecular interaction of phase molecules (CPA and NRTL equations).
- Additionally, although the performance of HydraFLASH, results were only slightly superior to the Multiphase flash. When averaged against all examined experimental data HydraFLASH exhibited remarkably better performance than the Multiphase flash at low temperatures where it is expected to differ in real-world industrial applications (e.g. at seabed conditions). Most likely due to more accurate values of hydrate reference properties used in the hydrate model calculated at low temperature (273.15 K).
- MF RKSA and MF CPA exhibit similar accuracy at low & high temperature/pressure due to the capability of NRTL (Non-Random-Two-Liquid) equation to describe non-ideality/Excess Gibbs as well as CPA. This fact will be further checked and confirmed for systems includes inhibitors and/or salts.

- HF & HF72 exhibit similar behavior/accuracy as association part in the CPA equation of state which explains a no effect of Cubic EoS type for the system of CO₂ at low and high temperature.
- Finally, based on the outcome of this study, we recommend the usage of HF or HF72 approaches for hydrate predictions and phase equilibria modeling.

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