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Hydrate Enthalpy of Dissociation from Statistical Thermodynamics

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HYDRATE ENTHALPY OF DISSOCIATION FROM STATISTICAL THERMODYNAMICS

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ENTALPIA DE DISSOCIAÇÃO DE HIDRATOS A PARTIR DA TERMODINÂMICA ESTATÍSTICA

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Dedico esta dissertação àqueles que estiveram ao meu lado durante esta etapa da minha vida.

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E ao imenso e possível oceano Ensinam estas Quinas, que aqui vês, Que o mar com fim será grego ou romano: O mar sem fim é português.

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Abstract

Statistical Thermodynamics was used to derive an expression for hydrate enthalpy of dissociation. From this expression, a parameter regression methodology was proposed in which calorimetric experiments were included along with cage occupancies, guest mole fraction and equilibrium condition experiments.

Since not all the experiments depend on the whole set of hydrate parameters, we developed a stepwise methodology that reduces parameter estimation problem to three simple sub-problems, with two of them being analytically solvable. The solution of the stepwise methodology is then the initial guess of the hydrate global parameter estimation that can be solved using a deterministic algorithm.

From the parameter estimation, we observed that the hard-core sphere parameter of the Kihara potential was not statistically significant in the case studied here. It was rejected with a significance degree of 5%, which lead to the use of the Lennard-Jones potential.

After estimating hydrate parameters for carbon dioxide and methane sI hydrates, we could relate hydrate enthalpy of dissociation to equilibrium conditions for this binary mixture. We found that the empirical law that states that enthalpy of dissociation of mixed hydrates increases with the increase of occupancy of the largest guest in the large cavity was verified only when the waterpoor fluid phase is a vapor. This means that fluid phases also have an important role in hydrate enthalpy of dissociation.

Resumo

Termodinâmica Estatística foi utilizada para deduzir uma expressão para a entalpia de dissociação de hidratos. A partir desta expressão, uma metodologia de estimação de parâmetros foi proposta, na qual experimentos calorimétricos foram incluídos, ao lado de dados de fração de ocupação de cavidades, fração molar de formadores e condições de equilíbrio.

Como nem todos os experimentos dependiam de todo o conjunto de parâmetros do modelo, propôs-se uma metodologia passo a passo, que reduz o problema de estimação de parâmetros de hidrato em três subproblemas, sendo que dois deles possuem solução analítica. A solução dada pela metodologia passo a passo é, então, utilizada como estimativa inicial do problema global de estimação de parâmetros, que pode ser resolvido usando um algoritmo determinístico.

Da estimação de parâmetros, foi observado que o parâmetro *hard-core* do potencial de Kihara não foi estatisticamente significativo no caso estudado. Ele foi rejeitado com um grau de significância de 5%, o que levou ao uso do potencial de Lennard-Jones.

Depois da estimação de parâmetros para hidratos sI do metano e do dióxido de carbono, a entalpia de dissociação de hidratos foi relacionada com as condições de equilíbrio para essa mistura binária. Verificou-se que a lei empírica que diz que entalpia de dissociação de hidratos mistos aumenta com o aumento da ocupação do maior formador na maior cavidade foi verificada apenas quando a fase fluida pobre em água é um vapor. Isso significa que as fases fluidas também têm um papel importante na entalpia de dissociação.

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List of Symbols

Latin Variables

- *a* Kihara Potential hard core parameter
- *A* Extensive internal energy
- *B* Heat capacity angular coefficient
- *C* Langmuir constant
- *Cp* Heat capacity at constant pressure
- *E* Extensive internal energy
- \overline{E} Molar internal energy
- \overline{E}_i Partial molar internal energy of component *i*
- f Fugacity
- *F* Cumulative Fisher distribution function
- F^{obj} Objective function
- $h_{i,j}$ Canonical partition function of molecule *j* in cavity *i*

 h_{Planck} Planck constant

- *H* Extensive enthalpy
- \overline{H} Molar enthalpy
- \overline{H}_i Partial molar enthalpy of component *i*
- \mathcal{H} Hamiltonian of the system
- *K* Kinetic energy
- $k_{\rm B}$ Boltzmann constant

- *m* Mass of a given particle
- n_{cav} Number of types of cavities in hydrate structure

 n_{guest} Number of guests

- $n_{\rm exp}$ Number of experiments
- $n_{\rm p}$ Number of parameters
- *N* Number of molecules
- $N_{\rm AV}$ Avogadro constant

p Momentum

- \underline{p} Momuntum vector or Matrix (Chapter 2) or Parameter vector (Chapter 3)
- p^* Optimal parameters vector
- *P* Pressure
- P_i Partial pressure of component j
- \underline{q} Vector of microscopic coordinates relative to the internal degrees of freedom of a molecule
- *Q* Canonical partition function
- <u>*r*</u> Microscopic positions vector or matrix
- r_{cav} Radius of a given cavity
- *R* Universal gas constants
- *T* Absolute temperature
- U Potential energy
- *V* Extensive volume

 \overline{V} Molar volume

w Spherically symmetrical intermolecular potential (Chapter 2) or Weights of global objective function (Chapter 3)

W Combinatorial term of the van der Waals and Platteeuw partition function

x Molar fraction

y Cage occupancy or guest molar fraction in hydrate phase

Greek Variables

- α Significance level
- β Product of temperature and the Boltzmann constant
- **Γ** Auxiliary variable
- δ Delta function
- ε Kihara and Lennard-Jones potential energy parameter
- $\theta_{i,i}$ Fractional occupancy of molecule *j* hydrate cavity *i*
- λ Activity
- μ Chemical potential
- ν Cavity per water molecules ratio
- Ξ Semi-grand canonical partition function
- σ Kihara and Lennard-Jones soft-core parameter
- σ_i Experimental uncertainty of experiment *i*
- ϕ_i Fugacity coefficient of component j
- Φ Ideal gas partition function without the volume term
- Ψ Semi-grand canonical-based thermodynamic potential

 Ω Microcanonical partition function

Latin abbreviations, superscripts, subscripts

0	Reference state
calc	Calculated value
diss	Dissociation
EL	Hydrate Empty Lattice
enc	Relative to the enclathration
exp	Experimental value
expd	Partition function depending on the expanded set of variables
g	Related to the global estimation or the global objective function
G	Gas
Н	Hydrate
H I	Hydrate Ice
H I IG	Hydrate Ice Pure ideal gas
H I IG int	Hydrate Ice Pure ideal gas Relative to the internal degrees of freedom of particles
H I IG int LW	Hydrate Ice Pure ideal gas Relative to the internal degrees of freedom of particles Liquid water
H I IG int LW PW	HydrateIcePure ideal gasRelative to the internal degrees of freedom of particlesLiquid waterPure water
H I IG int LW PW R	HydrateIcePure ideal gasRelative to the internal degrees of freedom of particlesLiquid waterPure waterResidual property
H I IG int LW PW R trans	HydrateIcePure ideal gasRelative to the internal degrees of freedom of particlesLiquid waterPure waterResidual propertyRelative to translation of particles

Operators

- Δ Finite difference operator
- ∇ Nabla differential operator
- ∇^2 Laplace operator

1. Introduction

1.1. Gas Hydrates Research Panorama

Gas hydrates are crystalline ice-like solid phases composed of a water lattice that encages guest molecules. The guest molecules capable of forming gas hydrates while in contact with water can be of distinct chemical natures. Hydrates of light hydrocarbons such as methane, ethane and propane, for example, have been widely studied by the specialized literature. Inorganic gases are also capable of forming hydrates and examples of guests molecules of that kind are nitrogen, carbon dioxide and hydrogen sulfide. As all the mentioned molecules occur abundantly in natural gas streams, the formation of gas hydrates is a safety concern in water-saturated systems in the oil and gas industry.

Gas hydrates have two structures that are more commonly observed, namely structure sI and structure sII. There is also structure sH. However, this structure has only been observed in laboratory conditions and it is less important from the flow assurance point of view. These structures possess cavities in which the guest molecule is encaged. The distinct types of cavities of each of the three structures are shown in .



Figure 1 - Cavities present in the different types of gas hydrate structures. Figure from Ballard (2002)¹.

Hammerschmidt² was the first author to report the plugging of natural gas transmission lines in 1934. Ever since this pioneer work, the focus of gas hydrate research has been driven to a pragmatic industry-oriented concern: the flow assurance problem that they represent. According to Sloan and Koh³, Hammerschmidt's work is a milestone, inaugurating modern hydrate research. Before 1934, hydrates were mostly regarded as scientific curiosity and, after that date, several authors (including Hammerschmidt himself²) made efforts to create empirical methods to predict hydrate formation^{4–7}.

It was only in 1957 that Barrer and Stuart proposed a phenomenological approach to predict hydrate formation conditions⁸. They were followed by van der Waals and Platteeuw in 1959⁹, who developed the model that is the most used today for the assessment of gas hydrate thermodynamic properties. Both models are based on Statistical Thermodynamics and they take much from the crystallographic advances that were made in the decades prior to their studies. In the 1950s, it was already known that there were at least two hydrate structures (namely, sI and sII)³ and such information was critical to the development of rigorous thermodynamic models. Being a phenomenological model, the van der Waals and Platteeuw model has advantages over the empirical ones: it can be readily extended to hydrates of multiple guests; and its extrapolations to conditions other than the ones used to estimate the model parameters are more reliable. Sloan and Koh consider the van der Waals and Platteeuw model to be one of the best examples of the use of Statistical Thermodynamics to calculate macroscopic properties, as it is one of the few models of the kind ingrained in current industrial practice³. Indeed, if one considers the works of Bazant and Trout¹⁰ or Klauda and Sandler¹¹, which calculate intermolecular potentials from Quantum Mechanics, and the work of Segtovich et al.¹², focused on flash calculations, one can see that the van der Waals and Platteeuw model bridges several modeling scales.

The van der Waals and Platteeuw model is based in a few main assumptions and they will be fully addressed in the Methodology chapter. Some modifications to their model have been proposed, being most of them related to the water-guest interaction. Some include the use of different intermolecular potentials¹³ and some other include different numbers of water shells in computing water-guest interaction¹⁴. Other authors have tried to get rid of one of the basic assumptions of the model, by considering a stretchable lattice^{15,16}. Belosludov *et al.*¹⁷ also tried to include guest-guest interactions to the model. However, all those efforts did not change the core Statistical Thermodynamics framework proposed by van der Waals and Platteeuw.

1.2. Gas Hydrate Deposits as a Source of Energy

Sloan and Koh³ also perceive another milestone in hydrate research. According to them, the timespan between the mid 1960 until today represents a third period in hydrate scientific literature, marked by the discovery of gas hydrate deposits in deep oceans, permafrost regions and extraterrestrial environments. One of the consequences of those discoveries was the opening of a new path for hydrate research. The aforementioned deposits could represent a new source of energy, since the amount of methane entrapped in them is indeed significant¹⁸. Collet and Kuuskra¹⁸ estimate that 20 million trillion cubic meters of natural gas are available in gas hydrates deposits worldwide.

Conventional methods of extracting natural gas from hydrate deposits are based on shifting equilibrium conditions either by depressurization (a shift in pressure), by thermal stimulation (a shift in temperature) or by inhibitor injection (a shift in chemical potential)¹⁹. However, the simple decomposition of gas hydrates might lead to geological instabilities, posing safety and environmental concerns²⁰. It should be noted that most of the guest molecules found in gas hydrates deposits (noticeably methane and carbon dioxide) are greenhouse gases.

The role and importance of gas hydrate deposits in world climate is still not clear. Dickens and Forswall noted in 2009^{21} that, despite being a major source of carbon-containing molecules, gas hydrates were still absent from most carbon cycle models at that time. Nonetheless, methane release from gas hydrates to the atmosphere could also have been responsible for several abrupt atmospheric changes in Earth's ancient history in the Permian/Triassic boundary and in the Paleocene/Eocene boundary, for instance²¹. The analysis of polar ice cores by de Garidel-Thoron *et al.*²² have also shown that massive releases of methane from the dissociation of naturally occurring gas hydrates could be responsible for the rapid climate changes that occurred more recently, in the last glacial episode. Those findings and ideas support the so called "clathrate gun" hypothesis²³: the dissociation of methane hydrates around 15 thousand years ago has resulted in global warming by a strong positive feedback process, in which the release of methane into the atmosphere led to higher temperatures and further hydrate decomposition. Hence, although hydrate

deposits might seem a promising alternative to resource-poor economies²⁴, one should be aware of their possible role in a rising world temperature scenario.

To avoid the release of greenhouse gases and maintain the geological stability of reservoirs, researchers have envisioned the production of methane from gas hydrate deposits by swapping it with carbon dioxide²⁵. This methodology would allow for both methane exploitation and carbon dioxide capture, as CO₂ would end up entrapped in the original gas hydrate deposits.

According to Goel²⁵, this technology would require investigation on the following topics: hydrodynamics of carbon dioxide injection and transport to the methane hydrate accumulation; thermodynamics of formation and dissociation of the hydrates of methane, carbon dioxide and their mixtures; and the kinetics of dissociation/formation of these hydrates and the conversion from methane hydrate to carbon dioxide hydrate. The understanding of the energetic aspects of swapping methane with carbon dioxide is especially important. The dissociation of gas hydrates is an endothermic process and the dissociation of CO₂ hydrates is more endothermic than that of methane. This means that during the swapping process, heat would be released by the forming of CO₂ hydrates and this could accelerate methane hydrate decomposition.

1.3. Industrial Applications of Gas Hydrates

Industrial applications of gas hydrates are also on the landscape of contemporary hydrate research. Three topics seem to be the center of research efforts, namely: natural gas storage as gas hydrates – the so-called solidified natural gas (SNG) technology; gas hydrates as secondary refrigerants in refrigeration cycles; and the use of gas hydrates in separation processes³.

SNG technology is based on the physical properties of gas hydrates. As hydrates are composed of guest molecules entrapped in water, they provide high gas storage capacity, they are non-explosive and they are safe to handle²⁶. According to Veluswamy *et al.*²⁶, SNG technology is environmentally benign and cost effective, being a viable alternative to liquefied natural gas, compressed natural gas or adsorbed natural gas. However, it has one main drawback: kinetics of hydrate formation is slow. In stirred-tank reactors, hydrate formation is limited by the mass transfer in the water-gas interface and, in unstirred systems, gas hydrates form a film that offers resistance to the further growth of the hydrate phase.

In refrigeration cycles, gas hydrates would be used to increase the cycle efficiency. Fournaison, Delahaye and Chatti²⁷ state that, to meet stricter emission regulations, the refrigeration industry ought to phase out primary refrigerants like CFCs and HCFs. One way to achieve such a goal is to design refrigeration cycles that use lower quantities of primary refrigerants. In order to do so, a secondary refrigerant fluid is needed and the use of slurries containing a material capable of undergoing phase changes is a convenient choice due to the latent heat of phase transition. Hence, hydrate slurries could be employed in those cycles and several studies have been focusing on understanding their thermodynamic and transport properties.

Separation processes using gas hydrates focus on two main areas: the purification of gaseous streams and the desalinization of water. The former application is based on separating gaseous components that have a higher tendency to form hydrates from those that do not, at certain thermodynamic conditions. One example would be the removal of carbon dioxide from flue gas or syngas, in which CO_2 would tend to form clathrates, while other gases such as hydrogen, nitrogen or sulfur oxides would not²⁸. Eslamimanesh *et al.*²⁹ also cite several examples of separation of gaseous streams. In the case of water desalination, a hydrate guest capable of forming hydrates at mild conditions would be put in contact with saltwater. After the hydrate formation, the fluid phase would be separated from the hydrate phase and the complete dissociation of the clathrates would provide salt free water, while the guest could be recycled.

1.4. Calorimetric Modeling of Hydrate Formation

In order to debottleneck the development of the hydrate applications cited before, calorimetric measurements have become popular techniques in the study of gas hydrates. They can be used to enlighten several aspects of hydrate formation and dissociation, as they provide information on thermodynamic equilibrium^{30–33}, on hydrate formation kinetics^{34,35} and on guest replacement³⁶. In 2018, several works focusing solely on experimentally assessing energetic aspects of formation, dissociation and guest replacement were published. Sun, Zhao and Yu³⁷ have measured the dissociation enthalpy of methane hydrates in salt solutions. Kumar *et al.*³⁸ have measured the enthalpy changes involved in the formation of mixed methane-tetrahydrofuran hydrates. Qing *et al.*³⁹ have measured dissociation enthalpies of semi-clathrates containing carbon

dioxide and methane. Mu and von Solms⁴⁰ focused on the swapping and dissociation of methane and carbon dioxide hydrates. These papers follow a trend from the previous years.

However, the modeling of such energy changes associated with gas hydrate has mostly been done by applying the Clapeyron or the Clausius-Clapeyron equations to equilibrium conditions of temperature and pressure^{30,41–43}. This is a somewhat limited approach, as it depends on numerically regressing values of enthalpy change for every possible gas hydrate mixture from its pressure-temperature diagram. In addition, it has been verified that hydrate formation is a coupled heat and mass transfer phenomenon⁴⁴. Therefore, in order to correctly model it, one has to take into account the heat involved in the formation or dissociation of these solids. This shows the importance of accurate determination of calorimetric properties.

One way to meet this demand is to use the widespread van der Waals and Platteeuw model⁹. Although it is mostly used for computing fugacities, the model derived by them is capable of relating all hydrate properties to those of pure water by using statistical thermodynamics and the hypothetical non-occupied hydrate phase (empty lattice) as a reference state. Here, we derive an expression for hydrate enthalpy of dissociation directly from the van der Waals and Platteeuw model. This expression is more useful than the Clausius equation, because it does not depend on regressing enthalpy changes from pressure-temperature diagrams, it does not introduce new empirical constants and it can be used with local equilibrium assumptions.

Using this expression, direct measurements of hydrate enthalpy of dissociation can also be included in hydrate parameter estimation. This is a non-trivial task as infinite combinations of parameters can yield satisfactory predictions of hydrate thermodynamic properties⁴⁵. Thus, in this work, we study the influence of calorimetric experiments as a new set of experiments in hydrate parameter estimation, along with cage occupancy and equilibrium (pressure *vs*. temperature) experiments. As a result, a new parameter estimation methodology is proposed and we apply it to simple and mixed sI hydrates of two components – methane and carbon dioxide.

This work is divided as follows. Firstly, in the Theoretical Background chapter, we take an in-depth look at the van der Waals and Platteeuw model. In the Methodology chapter, we derive an expression for hydrate enthalpy of dissociation. We also demonstrate how calorimetric measurements can be useful to enhance parameter estimation from hydrate equilibrium conditions. After addressing those issues, we enunciate the models used for each phase studied in this work (vapor, ice, liquid water and gas hydrate). We end the Methodology chapter by explaining the parameter regression procedure and enumerating experimental data used to fit the parameters. The quality of fit and the estimated parameters are discussed in the Results and Discussion chapter. We also present comments on the relations between hydrate enthalpy of dissociation, equilibrium conditions and occupancies. Finally, we present remarks in the Conclusion chapter.

2. Theoretical Background

2.1. The Development of 'Phenomenological Models

After the crystallographic determination of clathrate structures that has been carried in the late 1940s and early 1950s, the development of phenomenological models became finally possible, culminating in the publication of "Clathrate Solutions" by van der Waals and Platteeuw in 1959. The works of von Stackelberg *et al.*^{46–50}, Pauling and Marsh⁵¹ and Claussen^{52–54} in this period elucidated the two types of structure of gas hydrates, while several other works investigated the structures of other clathrates, such as those of hydroquinone lattice^{55–62}.

The idea that crystallographic work was fundamental to a rigorous hydrate model was already present in one of van der Waals' earliest works⁶³. Contrary to what it may seem, their well-known publication of "Clathrate Solutions"⁹ was not the earliest appearance of a thermodynamic partition function for clathrate compounds. The work from 1959 is actually a product of an extensive body of research that had been carried out throughout the whole 1950s, with the combined efforts of van der Waals, Platteeuw – these two working most of the time in collaboration – and Barrer and Stuart in 1957.

In 1953, van der Waals first published a canonical partition function for clathrates in the General Discussion section of volume 15 of Discussions of the Faraday Society⁶³. In that short piece, he states that, despite the availability of X-ray studies of clathrate compounds, little had been done on the development of a statistical theory for them. The partition function devised by him in that piece was very different from the well-known form of 1959. He developed an expression that depends on the number of "holes" in the clathrate and on the free volumes of all molecules, either host or guest (the "free volume" expression is a rather vague idea in this publication, but in van der Waals' later works it represents the configurational integral). However, he makes some statements that would ultimately lead to the formal assumptions of the 1959 model. According to him, it was reasonable to think that the free volume of host molecules would not depend on the nature of the guests. Furthermore, he establishes some fundamental requirements of the model-to-be:

(i) "Thermodynamically the hydrate must be described as a mixed crystal of a metastable water modification and a compound $mH_2O.1A^*$ having an incongruent melting point;

(ii) In the two-phase region hydrate + gas the equilibrium vapour pressure of the crystals should obey a Langmuir isotherm;

(iii) Along a three-phase line, where the hydrate is in equilibrium with two other phases, only one of the three variables T, P and y^{\dagger} is independent."

The follow-up of the 1953 work is the almost simultaneous publication of "Thermodynamic Properties of Quinol Clathrates"⁶⁴, by Platteeuw and van der Waals, and "The Statistical Mechanics of Clathrate Compounds"⁶⁵, by van der Waals. These two articles cited one another. In the former, a theoretical and experimental investigation of hydroquinone clathrates is carried out. Firstly, the authors obtain an expression for the clathrate vapor pressure. Then, they compare their results to the vapor pressure and the enthalpy change observed in the three-phase equilibrium of solid hydroquinone, vapor and hydroquinone clathrate for the binary system hydroquinone + argon. The enthalpy comparison is made via the Clausius-Clapeyron equation. The detailed description of the thermodynamic model used is given in the latter. In that work, van der Waals derives a partition function for hydroquinone clathrate, which possess only one type of cage. Here, we already see the core features of the 1959 model: we have the same basic assumptions and we see the use of the Lennard-Jones-Devonshire cell theory⁶⁶. The major difference lies in the ensemble used for the derivation, which, at that point, was the canonical one.

In 1957, Barrer and Stuart published a work entitled "Non-stoichiometric Clathrate Compounds of Water"⁸. In this work, they extend van der Waals' 1956 reasoning to gas hydrates, which have two distinct cage types. Barrer and Stuart's partition function already possesses a combinatorial analysis to deal with all possible cases of occupation and that is the main contribution they bring to the clathrate phenomenological models.

The next two works, published in 1958, were both authored by van der Waals and Platteeuw. In an experimental measurement of hydroquinone + argon clathrates, Platteeuw and

^{* &}quot;A" in the original work represents the guest

⁺ Mole fraction of one component

van der Waals verified that the vapor pressure of the guest is characterized by a Langmuir-type isotherm⁶⁷. The Langmuir-type isotherm for clathrates was predicted in the 1956 van der Waals' work, published in Transactions of the Faraday Society⁶⁵. In 1958, these authors also extended van der Waals' 1956 model to gas hydrates with the publishing of "Thermodynamic properties of gas hydrates"⁶⁸. In this paper, Platteeuw and van der Waals incorporated independently in their work some of the ideas that Barrer and Stuart had already brought up in 1957⁸. However, Barrer and Stuart's work was more general, as it accounted for several possible types of guests, while the Platteeuw and van der Waals' modification of their 1956 theoretical work only included different types of cages.

Then, in 1959, we have the publication of the van der Waals and Platteeuw model in the same form as it is currently used. In "Clathrate Solutions"⁹ they present a general formula, extendable to any number of guests or cavity types. It is also the first time that they present a semigrand canonical partition function, using the chemical potential of the guests as an independent variable. This time, their model was also capable of dealing with phase equilibrium with non-ideal fluid phases, as it was the first time that they described the guests by their fugacities. The analogy with the Langmuir-type isotherm also coined the expression "Langmuir constant", which is still used today to refer to the ratio of the enclathration configurational integral and $k_{\rm B}T$. In that same year, we also have the publication of "Thermodynamic Properties of Gas Hydrates II" by Platteeuw and van der Waals⁶⁹. This paper deals with the measurement of phase equilibria and the verification of their statistical thermodynamics framework. According to this paper, their model was capable of accounting for azeotropic-like behavior (congruent melting) in clathrate solutions.

Later works by these two authors did not bring great innovations to the phenomenological model. In 1959, they commented on the validity of the Clausius-Clapeyron equation application to the three-phase equilibrium lines of clathrate-containing systems⁷⁰. In 1961, van der Waals addressed the enclathration of large molecules, which would lead to a reduction of the number of possible states for the internal degrees of freedom of those molecules, in comparison to their free states⁷¹. In 1962, they presented an experimental technique relating the chemical potential difference between host-molecules in the hypothetical empty clathrate and in the real clathrate with measured clathrate composition⁷².

Hence, as we began this discussion, we see that the van der Waals and Platteeuw model is the embodiment of a series of works, of both theoretical and experimental nature, in the search for understanding clathrate thermodynamic properties. Figure 2 shows the major publications that deal with this subject in 1950s and early 1960s that are in some way related to the development of this model. In this figure, arrows point from one box to another to indicate that the paper at the base of the arrow cites the paper to which it points.

As we can see, apart from the crystallographic contributions made by Powel, von Stackelberg and others^{51,52,54}, who are heavily cited in van der Waals and Platteeuw's works, the only contributors other than these authors were Barrer and Stuart. Their paper, however, is of great influence, as indicated by several other papers of van der Waals or Platteeuw citing it. We also see that "Clathrate Solutions" works as a compilation of all acquired knowledge on clathrates phenomenology of the 1950s, as it reunites the results of almost all papers published before it. The 1956 "The Statistical Mechanics of Clathrate Compounds" and "Thermodynamic Properties of Quinol Clathrates" are also pivotal works, but all of the connections ultimately lead to "General Discussions", where it all began.



Figure 2 – Citation web of the 1950s contributions in clathrate phenomenological models.

2.2. The van der Waals and Platteeuw Assumptions

The van der Waals and Platteeuw model for clathrate compounds is based in three fundamental assumptions on the nature of clathrates. They are rewritten below, according to our interpretation of them.

- (a) The free energy of the clathrate comes from an *a priori* description of the host molecule lattice;
- (b) Guest molecules can only be located within clathrate cavities given the prior description of the lattice. In addition, there can be only one guest molecule per cavity in the lattice;
- (c) Interactions between guest molecules are neglected.

Assumption (a) was originally written in "Clathrate Solutions"⁹ as:

"The contribution of the Q molecules [host molecules] to the free energy is independent of the mode of occupation of the cavities."

An earlier and more complete appearance of the same assumption, even though specific to quinol clathrates, states that⁶⁵:

"The contribution of the quinol molecules to the total partition function is assumed to be the same for the empty β -quinol lattice as for the clathrate compound in which a fraction y of the holes is occupied, except for the fact that the quinol molecules determine the field in which the A^{\ddagger} molecules move. This implies that the vibrations and internal degrees of freedom of the quinol molecules are independent of y. Although this can never be strictly true, it is expected to be a reasonable approximation since the quinol molecules form a rigid structure through their hydrogen bonds and interact only weakly with non-polar A molecules. One should, however, exclude cases such as the compound between quinol and CO_2 , in which the trapped molecules have such dimensions that they seriously distort the β quinol lattice."

[‡] "A" in the original work represents the guest

The effect of this assumption is the separation of contributions of the host molecules from the rest of the system. By doing so, we will see that we can avoid a thorough description of the microscopic states of the empty lattice and postpone the problem of considering such states until we reach a macroscopic level. This is what has been done in the clathrate literature. The effect of this *a priori* structure in the properties of the whole system has been obtained by parameter estimation from equilibrium data. Hence, we interpret the original assumption as giving a certain priority to the host molecules in the counting of states, for we first devise an empty clathrate structure that can be in any possible state regardless of how a certain guest molecule will occupy which cage.

The original Assumption (b) is rather straightforward and it stresses our interpretation of Assumption (a). It states that:

"The encaged molecules are localized in the cavities and a cavity can never hold more than one solute molecule."

From this assumption, we see that the description of the host molecules is indeed primary, as the guest molecules can only exist within an *a priori* lattice structure. Therefore, we can say that the states in which the guest molecules can be are all the possible states, given the prior state of the host molecules. This assumption is also important as it limits the number of guest molecules per water molecule. As a corollary of (b), we know that there can only be as many guest molecules as there are cages. The impossibility of double or triple occupancy is also going to facilitate the computation of microstates of the system, but it will be one of the main limitations of this model, because experimental investigation has already shown that some guests are capable of occupying one cage with more than one molecule³.

Finally, we have Assumption (c), whose effect is the independence in the mode of occupation of guest molecules with respect to themselves. The original one from 1959 states that:

"The mutual interaction of the solute molecules is neglected."

In the same work, van der Waals and Platteeuw go further by explicitly mentioning its effects:

"The partition function for the motion of a solute molecule in its cage is independent of the number of types of solute molecules present."

This is an effect we will see when we consider the Hamiltonian of the system in Section 2.3.

van der Waals and Platteeuw make three additional assumptions. The first of the remainder assumptions is on the validity of Classical Statistics. The authors state that their framework is valid if Classical Statistics is valid – henceforth referred to as Assumption (d) –, i.e. Classical Statistical Mechanics is enough to predict relevant properties in conditions of interest, not requiring Quantum Statistical Mechanics calculations. This assumption is known to be valid for physical systems at not too low temperatures¹⁷.

The two remaining assumptions regard the Hamiltonian of an individual guest molecule. The authors state that the solute molecules can rotate freely in their cavities – henceforth referred to as Assumption (e). According to them, a consequence of this assumption is that the rotational partition function of guest molecules is the same of that in the ideal gas. This assumption is not made in the very first beginning of their statistical thermodynamics analysis, but in a later part of their work. This is probably because the expression derived by them from Assumptions (a), (b), (c) and (d) is valid no matter the rotational partition function. We will see that this assumption is extremely important when conceiving the molecular partition function for the individual guest molecule.

The last assumption – Assumption (f) –, which we will further explain in the next section, states that

"The potential energy of a solute molecule when at a distance r from the center of its cage is given by the spherically symmetrical potential w(r) proposed by Lennard-Jones and Devonshire."

This assumption reduces the number of microscopic coordinates that matter to the problem and, being a spherically symmetric potential, the only important coordinate is the relative displacement of the molecule from the center of the cavity. The late introduction of this assumption

in van der Waals and Platteeuw's work leads to some inconsistencies in later works that tried to extend their model. This is because the integration of this potential is performed from the center of the cavity to its limiting radius (r_{cav}), in which the latter can be considered a function of macroscopic variables that are not taken into account in van der Waals and Platteeuw's original work, as the authors only foresaw the use of a constant cage radius.

2.3. Considerations on the Hamiltonian of the System

From a microscopic point of view, the model assumptions impose several constrains to the Hamiltonian of the clathrate system (host molecule lattice and entrapped guest molecules). The first one is a common assumption in statistical thermodynamics. Firstly, we decompose the Hamiltonian of the system, \mathcal{H} , in two parts, being one of them accountable for the motion of the center of mass of the molecules, \mathcal{H}^{trans} , and another one accountable for the relative motion of molecular constituents with respect to that center of mass – the so-called internal degrees of freedom –, \mathcal{H}^{int} . We, then, have:

$$\mathcal{H} = \mathcal{H}^{\text{trans}} + \mathcal{H}^{\text{int}}$$
(2.1)

The translational Hamiltonian for the system is a function of the following variables:

$$\mathcal{H}^{\text{trans}} = \mathcal{H}^{\text{trans}}\left(\underline{p}_{N\times3}, \underline{r}_{N\times3}, N\right)$$
(2.2)

In which N represents the number of molecules present in the system. In the same equation, p and r represent the momentum and the position of an individual particle and all those values are grouped in the matrices \underline{p} and \underline{r} , respectively, which have N lines and 3 columns each. If we postulate a separable Hamiltonian with respect to momenta and positions, we would write:

$$\mathcal{H}^{\text{trans}} = K(\underline{p}_{N\times3}, N) + U(\underline{r}_{N\times3}, N)$$
(2.3)

In this equation, K represents the kinetic energy of the particles and U represents their potential energy. The expression of K used here is the classical one, which depends only on the momentum of the particles and the number of molecules in the system. K is, then, expressed in Equation (2.4) in which m_i is the mass of particle i.

$$K\left(\underline{p}_{N\times3}, N\right) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i}$$
(2.4)

Deriving an expression for the potential energy is more complicated as the assumptions of the van der Waals and Platteeuw model have direct consequences on U. As stated earlier, an *a priori* description of the empty clathrate lattice in needed before the inclusion of guest molecules in the modeling. This means that the potential energy of the empty lattice is not a function of the positions of the guests. In addition, the guest molecules do not interact with each other, which means that the only microscopic coordinates on which their potential energy depends are the position of water molecules and the position of each individual guest molecule. Hence, the potential energy of the whole system can be separated into two contributions: one related to the empty lattice (EL) and the other one related to the enclathration of individual guest molecules (enc), as in the following equation.

$$U(\underline{r}_{N\times3}, N) = U^{\mathrm{EL}}(\underline{r}_{N_{\mathrm{w}}\times3}, N_{\mathrm{w}}) + \sum_{j=1}^{N_{\mathrm{guest}}} U_{j}^{\mathrm{enc}}(\underline{r}_{j}_{1\times3}, \underline{r}_{N_{w}\times3}, N_{\mathrm{w}})$$
(2.5)

The potential energy of the empty lattice is not further developed in the van der Waals and Platteeuw model. However, further simplifications in the enclathration term need to be made considering the other assumptions of the model. In order to make the enclathration energy depend only on microscopic coordinates of the guests, all guest-host interactions are combined into a mean potential function. This takes away the dependency of U_j^{enc} with microscopic positions of water molecules. However, we are now working with mean host positions that can be obtained from macroscopic properties. Hence, from now on, U_j^{enc} will depend on the extensive volume of the clathrate (V). It will still be a function of the total number of host molecules though, both because we consider the contribution of all of them in the mean guest-host potential function and because their mean distance to the guests depends on the clathrate molar volume with respect to host molecules (\overline{V}). Now, the only important microscopic coordinates are the distance between the guest molecule and the center of the cavity (r) and the radius of the cavity (r_{cav}). This last variable is important, because the guest molecules can only be positioned inside one cavity or another, thus replacing the absolute dependency on space coordinate to a relative dependency coordinate with respect to a given cavity center. A further explanation of its role can be found in Section 2.9.
However, in clathrates, cavities can be of several types and this would lead to different potential functions. Therefore, not only the potential function varies from cavity to cavity, but also the total number of guest molecules in each type of cavity. We, then, introduce variables $N_{i,j}$ representing the number of molecules *j* in cavities of type *i*.

$$U\left(\underline{r}_{N_{w}\times3},\underline{r}_{n_{cav}\times n_{guests}\times N_{i,j}},\underline{r}_{cav},N,V\right) = U^{EL}\left(\underline{r}_{N_{w}\times3},N_{w}\right) + \sum_{i=1}^{n_{cav}}\sum_{j=1}^{n_{guest}}\sum_{k=1}^{N_{i,j}}U_{i,j,k}^{enc}\left(r_{i,j,k},r_{cav,i},V,N_{w}\right)$$
(2.6)

Finally, the complete translational Hamiltonian of the clathrate system following the van der Waals and Platteeuw assumptions is obtained:

$$\mathcal{H}^{\text{trans}} = \sum_{i=1}^{N_{w}} \frac{p_{i}^{2}}{2m_{i}} + U^{\text{EL}}\left(\underline{r}_{N_{w}\times3}, N_{w}\right) + \sum_{i=1}^{N_{\text{guest}}} \frac{p_{i}^{2}}{2m_{i}} + \sum_{i=1}^{n_{\text{cav}}} \sum_{j=1}^{n_{\text{cav}}} \sum_{k=1}^{N_{i,j}} U^{\text{enc}}_{i,j,k}\left(\underline{r}_{k_{1\times3}}, r_{\text{cav},i}, V, N_{w}\right)$$
(2.7)

Then, we can identify the Hamiltonian of two subsystems:

$$\mathcal{H}^{\text{trans-EL}} = \sum_{i=1}^{N_{\text{w}}} \frac{p_i^2}{2m_i} + U^{\text{EL}}\left(\underline{r}_{N_{\text{w}}\times3}, N_{\text{w}}\right)$$
(2.8)

$$\mathcal{H}^{\text{trans-enc}} = \sum_{i=1}^{N_{\text{guest}}} \frac{p_i^2}{2m_i} + \sum_{i=1}^{n_{\text{cav}}} \sum_{j=1}^{n_{\text{guest}}} \sum_{k=1}^{N_{i,j}} U_{i,j,k}^{\text{enc}} \left(\underline{r_k}_{1\times 3}, r_{\text{cav},i}, V, N_w \right)$$
(2.9)

If we define a new Hamiltonian for each type guest molecule in each type of cavity, we have:

$$\mathcal{H}_{i,j,k}^{\text{trans-enc}} = \frac{p_i^2}{2m_i} + U_{i,j,k}^{\text{enc}} \left(\underline{r_k}_{1\times 3}, r_{\text{cav},i}, V, N_w \right)$$
(2.10)

$$\mathcal{H}^{\text{trans}} = \mathcal{H}^{\text{trans-EL}} + \mathcal{H}^{\text{trans-enc}} = \mathcal{H}^{\text{trans-EL}} + \sum_{i=1}^{n_{\text{cavities}}} \sum_{j=1}^{n_{\text{guest}}} \sum_{k=1}^{N_{i,j}} \mathcal{H}^{\text{trans-enc}}_{i,j,k}$$
(2.11)

As we separated the molecules of our system into two groups, namely those pertaining to the empty lattice structure, and those pertaining to the guest molecule group, we can also separate the Hamiltonian for their molecular internal motions, if we postulate that the internal motion of a given molecule does not influence the internal motion of another one (independent degrees of freedom). Hence, we have the complete Hamiltonian of the system:

$$\mathcal{H} = \mathcal{H}^{\text{trans}} + \mathcal{H}^{\text{int}} = \mathcal{H}^{\text{EL}} + \mathcal{H}^{\text{enc}}$$
(2.12)

$$\mathcal{H} = \mathcal{H}^{\text{trans-EL}} + \mathcal{H}^{\text{int-EL}} + \sum_{i=1}^{n_{\text{cavities}}} \sum_{j=1}^{n_{\text{guest}}} \sum_{k=1}^{N_{i,j}} \left(\mathcal{H}^{\text{trans-enc}}_{i,j,k} + \mathcal{H}^{\text{int-enc}}_{j,k} \right)$$
(2.13)

From this derivation, we can see that it is very convenient to formulate the problem of describing clathrate thermodynamic properties as two subproblems: the empty lattice and the enclathration of a guest molecule. We will also see that the van der Waals and Platteeuw model works by obtaining the thermodynamic properties of real clathrates from two distinct references: the ideal gas (internal degrees of freedom of the guest molecules) and a hypothetical empty clathrate structure composed of only host molecules (water in the case of hydrates).

2.4. The Microcanonical Partition Function

To obtain the microcanonical partition function, we need to count the number of possible microscopic states in which the system can be with a given set of number of molecules (N), internal energy (E) and volume (V). Every combination of positions and momenta of particles corresponds to a microstate of the system and each microstate has its corresponding Hamiltonian. Hence, possible states are those in which the Hamiltonian equals the established internal energy of the system. This reasoning is put in a mathematical form by the following expression:

$$\Omega(\underline{N}, V, E) = \sum_{k=1}^{\infty} \delta[\mathcal{H}_{k}(\underline{N}, V) - E]$$
(2.14)

In this equation, δ represents a function that is either zero or one, being the latter when the bracketed expression is zero. The expression means that for all possible Hamiltonians, the only ones that are going to be counted are those that are equal to the internal energy specified for the system. Given the Hamiltonian expression in Equation (2.12), we can write:

$$\Omega(\underline{N}, V, E) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \delta(\mathcal{H}_{k}^{\text{EL}} + \mathcal{H}_{l}^{\text{enc}} - E)$$
(2.15)

Hence, despite our capacity of describing the system with independent Hamiltonian contributions, we have only one fixed internal energy for the system. Therefore, if one tries to devise a partition function for the whole system based on the number of empty lattice microstates

and the number of microstates of the guests, an expression of the following kind would have to be written:

$$\Omega(\underline{N}, V, E) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \Omega^{\text{EL}} (E_k^{\text{EL}}, N_w, V) \Omega^{\text{enc}} (E_l^{\text{enc}}, \underline{N}_{\text{guest}}, N_w, V) \delta(E_k^{\text{EL}} + E_l^{\text{enc}} - E)$$
(2.16)

In Expression (2.16), we see that the number of states in which the clathrate can be is a combination of independent configurations of the empty lattice (Ω^{EL}) and the guests (Ω^{enc}). However, those combinations must meet the condition that the internal energy of the clathrate equals the sum of the internal energy of the empty lattice (E_k^{EL}) and the internal energy of enclathration (E_l^{enc}). Therefore, despite having two distinct contributions, the system is still described by variables <u>N</u>, V, E.

Here, we do not develop the expression for the number of states of the empty lattice (Ω^{EL}), as we did not develop an expression for U^{EL} . On the other hand, we can calculate the microscopic aspects of the guests in the clathrate phase.

Given that the empty lattice follows an *a priori* crystallographic structure containing distinct cavities and that Assumption (b) is valid, a less usual combinatorial analysis is needed to obtain an expression for Ω^{enc} . First, for actually counting the number of states, we will have to use variables $N_{i,j}$ that represent the number of guest molecules of type *j* present in cavities of type *i*. The partition function we derived in Expression (2.16) is not a function of such variables. Hence, we need to add them to the problem consistently with the original \underline{N}, V, E set of variables. To do so, the sum of $N_{i,j}$ in all cavities has to be equal to the original variable N_j and this impose a restriction to the partition function $\delta\left(\sum_{i=1}^{n_{exv}} N_{i,j} - N_j\right)$. We, then, split the internal energy of the system into E^{EL} and E^{enc} , as:

$$\Omega^{\text{enc}}\left(E_{l}^{\text{enc}},\underline{N}_{\text{guest}},N_{\text{w}},V\right) = \left[\sum_{N_{1,1}=0}^{\infty}\sum_{N_{1,2}=0}^{\infty}\cdots\sum_{N_{1,n_{\text{guest}}}=0}^{\infty}\cdots\sum_{N_{n_{\text{cav}},n_{\text{guest}}}=0}^{\infty}\left[\Omega^{\text{enc}}\left(E_{l}^{\text{enc}},\underline{N}_{n_{\text{cav}}\times n_{\text{guest}}},N_{\text{w}},V\right)\times\right]\right]$$

$$\left[\prod_{j=1}^{n_{\text{guest}}}\left[\delta\left(\sum_{i=1}^{n_{\text{cav}}}N_{i,j}-N_{j}\right)\right]\right]\right]$$
(2.17)

The chained summations of Equation (2.17) are represented in the following compact notation.

$$\Omega^{\text{enc}}\left(E_{l}^{\text{enc}}, \underline{N}_{\text{guest}}, N_{\text{w}}, V\right) = \sum_{\underline{N}}^{\infty} \left[\Omega^{\text{enc}}\left(E_{l}^{\text{enc}}, \underline{N}_{n_{\text{cav}} \times n_{\text{guest}}}, N_{\text{w}}, V\right) \prod_{j=1}^{n_{\text{guest}}} \left[\delta\left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j} - N_{j}\right)\right]\right]$$
(2.18)

Now we come up with an expression for the cavity-dependent term of enclathration of guest molecules (Ω^{enc}), given its variables E_j^{enc} , $\underline{N}_{n_{cav} \times n_{guest}}$, V. Here, we use some of the van der Waals and Platteeuw's assumptions. Given that guests can only exist within cavities and that there can only be one guest per cavity, we see that the addition of a guest molecule diminishes the number of possibilities of addition for the next one. Furthermore, cavities have a known structure and each of them can be identified as pertaining to a specified type. Guest-guest interactions are neglected and the Hamiltonian of a single guest molecule depends only on the distance between the guest and the center of the cavity (r); the mean radius of the cavity it is in (r_{cav}); and macroscopic variables common to all guests (V, N_w). Then, there exists a variable $\Omega^{guest}_{i,j}$ that represents the number of states in which a guest of type j can be in a cavity of type i. Therefore, we have that:

$$\Omega^{\text{enc}}\left(E_{l}^{\text{enc}}, \underline{N}_{n_{\text{cav}} \times n_{\text{guest}}}, N_{\text{w}}, V\right) = W \prod_{i=1}^{n_{\text{cav}}} \prod_{j=1}^{N_{i,j}} \Omega^{\text{guest}}_{i,j}\left(E_{i,j,l}^{\text{guest}}, N_{\text{w}}, V\right)$$
(2.19)

In the Expression (2.19), *W* accounts for the number of ways in which guests can be placed in clathrate cavities and $\Omega^{\text{guest}}_{i,j}$, as stated before, represents the number of states of such guests within the cavities.



Figure 3 – Schematic representation of clathrate compounds. (a) Clathrate of one type of guest molecules and one type of cavity; (b) Clathrate of one type of guest molecules and two types of cavities; and (c) Clathrate of two types of guest molecules and two types of cavities.

The *W* term of the right-hand side is developed as follows. If the lattice had only one type of cavity and only one type of guest would be present, like the scheme in Figure 3-a, the number of states in which guests could be would be the simple combination of number of cavities and the number of molecules of the guest.

$$W = \begin{pmatrix} N_{\text{cav}} \\ N_{\text{guests}} \end{pmatrix} = \frac{N_{\text{cav}}!}{N_{\text{guests}}! (N_{\text{cav}} - N_{\text{guests}})}$$
(2.20)

However, if we want to move towards a more general expression, we need to add another type of cavity in the empty lattice. Figure 3-b shows a scheme of guests of the same type entrapped in a lattice of two kinds of cavities. In this case, two distinct combinations exist: one related to large cavities and another one related to the small cavities. This leads to:

$$W = \begin{pmatrix} N_{\text{cav1}} \\ N_{\text{guests, cav1}} \end{pmatrix} \begin{pmatrix} N_{\text{cav2}} \\ N_{\text{guests, cav2}} \end{pmatrix} = \frac{N_{\text{cav1}}!}{N_{\text{guests, cav1}}! (N_{\text{cav1}} - N_{\text{guests, cav1}})} \frac{N_{\text{cav2}}!}{N_{\text{guests, cav2}}! (N_{\text{cav2}} - N_{\text{guests, cav2}})}$$
(2.21)

It should be noted that in this expression, the total number of guest molecules has been split in the number of molecules that occupy cavities of type 1 and the number of molecules that occupy cavity 2. The generalization of this expression to a number n_{cav} of cavities furnishes the following expression:

$$W = \binom{N_{\text{cav1}}}{N_{\text{guests, cav1}}} \times \binom{N_{\text{cav2}}}{N_{\text{guests, cav2}}} \times \cdots \binom{N_{\text{cav,ncav}}}{N_{\text{guests, ncav}}} = \prod_{i=1}^{n_{\text{cav}}} \binom{N_{\text{cav, }i}}{N_{\text{guests, }i}}$$
(2.22)

However, in nature, there exist clathrates of different types of guest molecules. Hence, one final reasoning is needed in order to find the most general expression of this kind, given the model assumptions. Figure 3-c shows a scheme for hydrates of two different cavities and two different kinds of guests. In this scenario, one needs to have in mind that the presence of guest 1 in cavity type 1 diminishes the number of available cavities of type 1 to all guests, 1 and 2. Hence, Expression (2.21) becomes:

$$W = \frac{N_{\text{cav1}}!}{N_{\text{guest1, cav1}}! (N_{\text{cav1}} - N_{\text{guests, cav1}})} \frac{N_{\text{cav1}}!}{N_{\text{guest2, cav1}}! (N_{\text{cav1}} - N_{\text{guests, cav1}})} \times \frac{N_{\text{cav2}}!}{N_{\text{guest1, cav2}}! (N_{\text{cav2}} - N_{\text{guests, cav2}})} \frac{N_{\text{cav2}}!}{N_{\text{guest2, cav2}}! (N_{\text{cav2}} - N_{\text{guests, cav2}})}$$
(2.23)

In this expression, $N_{\text{guests, cav}}$ represents the sum of all guest molecules in each cavity type. The generalization of this expression to n_{cav} and n_{guests} yields:

$$W = \prod_{j=1}^{n_{\text{guest}}} \prod_{i=1}^{n_{\text{cav},i}} \frac{N_{\text{cav},i}!}{N_{i,j}! \left(N_{\text{cav},i} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j} \right)!}$$
(2.24)

Here, the subscript "guests" has been omitted and we reintroduce variables $N_{i,j}$. This expression is finally rearranged into Expression (2.25).

$$W\left(\underline{\underline{N}}\right) = \prod_{i=1}^{n_{\text{cav}}} \frac{N_{\text{cav},i}!}{\left[\left(N_{\text{cav},i} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right)!\right] \prod_{j=1}^{n_{\text{guests}}} N_{i,j}!}$$
(2.25)

However, the number of cavities is not a convenient variable here. Therefore, we must introduce new variables to relate it to the number of host molecules. Given that the empty lattice possesses a fixed crystalline structure, we know how many host molecules are present and how many cavities they can form, so we introduce the following variable:

$$\nu_i = \frac{N_{\text{cav},i}}{N_{\text{w}}}$$
(2.26)

Hence, Expression (2.25) becomes:

$$W = \prod_{i=1}^{n_{cav}} \frac{(\nu_i N_w)!}{\left[\left(\nu_i N_w - \sum_{j=1}^{n_{guests}} N_{i,j} \right)! \right] \prod_{j=1}^{n_{guests}} N_{i,j} !}$$
(2.27)

We also introduce the variable W_i that will be important later:

$$W_{i} = \frac{(\nu_{i} N_{w})!}{\left[\left(\nu_{i} N_{w} - \sum_{j=1}^{n_{guests}} N_{i,j}\right)!\right] \prod_{j=1}^{n_{guests}} N_{i,j}!}$$
(2.28)

Finally, we consider the number of possible internal configurations of guests of different types in the two types of cavities $(\Omega_{i,j})$ at a given internal energy *E*:

$$\Omega^{\text{enc}}\left(E_{l}^{\text{enc}}, \underline{N}_{n_{\text{cav}} \times n_{\text{guest}}}, V\right) = \prod_{i=1}^{n_{\text{cav}}} \left[\frac{\left(\nu_{i} N_{\text{w}}\right)!}{\left(\nu_{i} N_{\text{w}} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right)!} \prod_{j=1}^{n_{\text{guests}}} \Omega_{j=1}^{\text{guest}} \Omega_{i,j,l}^{\text{guest}}\right]$$
(2.29)

We can now combine it to the expression derived for the empty lattice and we arrive at the number of states for the whole clathrate as a function of the number of guests *j*.

$$\Omega(\underline{N}, V, E) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \sum_{\underline{N}}^{\infty} \left\{ \Omega^{\text{EL}}(E_{k}^{\text{EL}}, N_{w}, V) \Omega^{\text{enc}}(E_{l}^{\text{enc}}, \underline{N}_{n_{\text{cav}} \times n_{\text{guest}}}, N_{w}, V) \times \left\{ \delta(E_{k}^{\text{EL}} + E_{l}^{\text{enc}} - E) \prod_{j=1}^{n_{\text{guest}}} \left[\delta\left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j} - N_{j}\right) \right] \right\} \right\}$$

$$(2.30)$$

Alternatively, by expanding Ω^{enc} with Equation (2.28):

$$\Omega(\underline{N}, V, E) = \left\{ \begin{array}{l} \Omega^{\text{EL}}\left(E_{k}^{\text{EL}}, N_{w}, V\right) \times \\ \prod_{i=1}^{\infty} \sum_{l=1}^{\infty} \sum_{\underline{N}}^{\infty} \left\{ \prod_{i=1}^{n_{\text{cav}}} \left[\frac{(v_{i}N_{w})!}{(v_{i}N_{w} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j})!} \prod_{j=1}^{n_{\text{guests}}} N_{i,j}! \prod_{j=1}^{N_{\text{guest}}} \Omega^{\text{guest}}_{i,j} \left(E_{i,j,l}^{\text{guest}}, N_{w}, V\right) \right] \times \right\}$$

$$\left\{ \delta\left(E_{k}^{\text{EL}} + \sum_{i=1}^{n_{\text{cav}}} \sum_{j=1}^{n_{\text{guest}}} E_{i,j,l}^{\text{guest}} - E\right) \prod_{j=1}^{n_{\text{guest}}} \left[\delta\left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j} - N_{j}\right) \right] \right] \right\}$$

$$\left\{ \left\{ \left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j} - N_{j}\right) \right\} \right\}$$

$$\left\{ \left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j} - N_{j}\right) \right\} \right\}$$

2.5. The Canonical Partition Function

The microcanonical ensemble is not the most convenient to treat clathrate systems. Therefore, we use the canonical partition function, with the following transformation⁷³:

$$Q(\beta, \underline{N}, V) = \sum_{q}^{\infty} \Omega(E_q, \underline{N}, V) e^{-\beta E_q}$$
(2.32)

In which β represents $1/k_{\rm B}T$ and *E* represents the energy of a state *q*, one of the independent variables of the microcanonical ensemble. Hence, we obtain the following by using the clathrate microcanonical partition function in a condensed form – Expression (2.16) – into Expression (2.33):

$$Q(\beta, \underline{N}, V) = \sum_{q=1}^{\infty} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \left[\begin{array}{c} \Omega^{\text{EL}} \left(E_k^{\text{EL}}, N_w, V \right) \Omega^{\text{enc}} \left(E_l^{\text{enc}}, \underline{N}_{\text{guest}}, N_w, V \right) \times \\ \delta \left(E_k^{\text{EL}} + E_l^{\text{enc}} - E_q \right) \exp \left(-\beta E_q \right) \end{array} \right]$$
(2.33)

Since there are only two terms that depend on E_q in Expression (2.33), we can pull independent terms out of the inner summations:

$$Q(\beta, \underline{N}, V) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \left[\sum_{q=1}^{\infty} \delta(E_k^{\text{EL}} + E_l^{\text{enc}} - E_q) \exp(-\beta E_q) \right]$$
(2.34)

The sum in index q will only effectively count the terms for which $E_k^{\text{EL}} + E_l^{\text{enc}} = E_q$, as a result from the δ function. Hence, it is equivalent to removing the summation and implementing the substitution:

$$Q(N,V,\beta) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \Omega^{\text{EL}} \left(E_k^{\text{EL}}, N_w, V \right) \Omega^{\text{enc}} \left(E_l^{\text{enc}}, \underline{N}_{\text{guest}}, N_w, V \right) \exp \left[-\beta \left(E_k^{\text{EL}} + E_l^{\text{enc}} \right) \right]$$
(2.35)

Then, because Ω^{EL} and Ω^{enc} are independent, the canonical partition can be split into two partition functions: the canonical partition function of the empty lattice and the canonical partition function of the guests.

$$Q(N,V,\beta) = \left[\sum_{k=1}^{\infty} \Omega^{\text{EL}} \left(E_k^{\text{EL}}, N_w, V\right) \exp\left(-\beta E_l^{\text{EL}}\right)\right] \times \left[\sum_{l=1}^{\infty} \Omega^{\text{enc}} \left(E_l^{\text{enc}}, \underline{N}_{\text{guest}}, N_w, V\right) \exp\left(-\beta E_l^{\text{enc}}\right)\right]$$
(2.36)

Finally, we arrive at:

$$Q(\underline{N}, V, \beta) = Q^{\text{EL}}(N_{\text{w}}, V, \beta) \times Q^{\text{enc}}(\underline{N}_{\text{guests}}, N_{\text{w}}, V, \beta)$$
(2.37)

The same reasoning is valid for each individual guest molecule, given the independence of their contributions from the Hamiltonians and, thus, of their internal energy contributions. Here, we introduce a partition function for a system of a guest molecule of type *j* subject to the field generated by a cage of type *i*, which will be henceforth represented by $h_{i,j}$ as in Expression (2.38). By doing so, we can then write the complete canonical partition function for the clathrate – Expression (2.39) –, relating that partition function to the Hamiltonian contribution of the enclathration of the molecule.

$$h_{i,j}\left(\beta, V, N_{w}\right) = \sum_{q=1}^{\infty} \Omega_{i,j,q} \exp\left(-\beta \mathcal{H}_{i,j,q}^{\text{enc}}\right)$$
(2.38)

$$Q(\underline{N}, \beta, V) = \begin{cases} Q^{\text{EL}}(N_{\text{w}}, \beta, V) \times \\ \prod_{i=1}^{\infty} \begin{cases} \frac{Q^{\text{EL}}(N_{\text{w}}, \beta, V) \times \\ \left[\frac{1}{\left(v_{i}N_{\text{w}}\right)!} \prod_{j=1}^{n_{\text{guests}}} N_{i,j}\right]! \prod_{j=1}^{n_{\text{guests}}} N_{i,j}! \prod_{j=1}^{n_{\text{guests}}} h_{i,j}(\beta, V, N_{\text{w}}) \end{bmatrix} \times \\ \prod_{j=1}^{n_{\text{guest}}} \left[\delta\left(\sum_{i=1}^{n_{\text{cav}}} N_{i,j,k} - N_{j}\right)\right] \end{cases}$$
(2.39)

The canonical partition function as a function of the expanded variable set (Q_{expd}) would, then, be:

$$Q_{\text{expd}}\left(N_{\text{w}}, \underline{M}_{n_{\text{cav}} \times n_{\text{guest}}}, \beta, V\right) = Q^{\text{EL}}\left(N_{\text{w}}, \beta, V\right) \prod_{i=1}^{n_{\text{cav}}} \left[\frac{\left(v_{i}N_{\text{w}}\right)!}{\left(v_{i}N_{\text{w}} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right)! \prod_{j=1}^{n_{\text{guests}}} N_{i,j}!} \prod_{j=1}^{N_{\text{guests}}} h_{i,j}\left(\beta, V, N_{\text{w}}\right)\right]$$
(2.40)

With the knowledge that $h_{i,j}$ is the same for every molecule of type *j* in any cage of type *i* we can rewrite the product of these functions as a product in number of guest types (n_{guests}), instead of number of guest molecules (N_{guests}).

$$\prod_{j=1}^{N_{\text{guests}}} h_{i,j}(\beta, V, N_{\text{w}}) = \prod_{j=1}^{n_{\text{guests}}} \left[h_{i,j}(\beta, V, N_{\text{w}}) \right]^{N_{i,j}}$$
(2.41)

This expression is equivalent to the canonical partition function presented by van der Waals and Platteeuw's original work; with the relation between the Helmholtz energy and the canonical partition function:

$$\ln Q = -\frac{A}{k_{\rm B}T} = -\beta A \tag{2.42}$$

$$Q_{\text{expd}}\left(N_{\text{w}}, \underline{N}_{n_{\text{cav}} \times n_{\text{guest}}}, \beta, V\right) = \exp\left(-\beta A^{\text{EL}}\right) \prod_{i=1}^{n_{\text{cav}}} \left[\frac{\left(v_{i}N_{\text{w}}\right)!}{\left(v_{i}N_{\text{w}} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right)!} \prod_{j=1}^{n_{\text{guests}}} N_{i,j}! \prod_{j=1}^{n_{\text{guests}}} h_{i,j}!\right]$$
(2.43)

The partition function, expressed in Equation (2.43), is analogous the one obtained by Barrer and Stuart in 1957. The authors proceeded to the derivation of macroscopic thermodynamic properties by differentiation of the Helmholtz energy expression obtained from it with respect to the independent variables of the function.

2.6. The Semi-Grand Canonical Partition Function

The independent variables chosen by van der Waals and Platteeuw to describe clathrates were temperature (T), volume (V), number of molecules in the lattice (N_w) and the absolute activities of the guest species $(\lambda_i)^{73}$. Respecting the restrictions of thermodynamics (e.g.: conjugated variables such as pressure and volume cannot be both specified at the same time and so on), this set of variables is the most convenient one. One of the reasons for this is the easy obtention of an average N_i from the differentiation of the semi-grand canonical partition function with respect to λ_i . Obtaining the value of λ_i from the canonical partition function would require the differentiation of that function with respect to N_j , which is actually an integer value. Hence, a transformation would be required in order to obtain the real average value of N_i , instead of the integer N_i . Apart from that, we also have some other conveniences that are pointed out here. Temperature is one of the intensive variables involved in phase equilibrium criteria. As the volume is an independent variable in the defined partition function and guests are encaged in the predefined clathrate structure, the volume of the empty lattice reference is the same as that of the real clathrate. The empty lattice and the clathrate have a known and well-characterized crystalline structure with fixed number of molecules. Finally, clathrates are non-stoichiometric compounds, because the number of guest molecules that can stabilize the clathrate structure varies with other thermodynamic properties. However, at equilibrium conditions, the chemical potential of guest species will be the same in the fluid phases and in the clathrate structure.

The only difference between the convenient variables and the ones in the partition function derived before – Equation (2.39) – is related to the guests. In the canonical partition function, their influence is being considered by the number of molecules entrapped. Here, we would like to express their contribution in terms of absolute activity as van der Waals and Platteeuw defined:

$$\lambda_{j} = \exp\left(\frac{\mu_{j}}{k_{\rm B}T}\right) = \exp\left(\beta\mu_{j}\right)$$
(2.44)

In this expression, μ_j is the absolute chemical potential of guest species *j*. The semi-grand canonical partition function can be obtained from the canonical partition function by the following expressions for a single component⁷³:

$$\Xi(\beta, V, \lambda) = \sum_{N=0}^{\infty} Q(\beta, V, N) \lambda^{N}$$
(2.45)

For a multicomponent system of $N_{\text{guest},j}$ molecules of type *j* and a total number of guests n_{guest} , like the one we have here, we have the following generalization.

$$\Xi(\beta, V, \underline{\lambda}) = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \cdots \sum_{N_{n_{\text{guests}}}}^{\infty} \prod_{j=1}^{n_{\text{guest}}} \mathcal{Q}(\beta, V, \underline{N}) \lambda_j^{N_j} = \sum_{\underline{N}}^{\infty} \prod_{j=1}^{n_{\text{guest}}} \mathcal{Q}(\beta, V, \underline{N}) \lambda_j^{N_j}$$
(2.46)

For the clathrate system, however, we are only willing to transform variables related to the guests. Hence, if we substitute the expression for $Q(\beta, V, \underline{N})$ from Expression (2.39) into Expression (2.46), we arrive at:

$$\Xi(\beta, V, N_{\rm w}, \underline{\lambda}_{\rm guest}) = \sum_{\underline{N}=0}^{\infty} \sum_{\underline{N}}^{\infty} \prod_{j=1}^{n_{\rm guest}} \prod_{i=1}^{n_{\rm cav}} Q^{\rm EL} W_i \delta\left(\sum_{i=1}^{n_{\rm cav}} N_{i,j} - N_j\right) \lambda_j^{N_j} h_{i,j}^{N_{i,j}}$$
(2.47)

In Expression (2.47) we see that the delta function and the sum in \underline{N} can vanish if we substitute N_j terms for $\sum_{i=1}^{n_{eav}} N_{i,j}$, in a similarly to what we did in the microcanonical partition function derivation. Hence, we obtain Expression (2.48).

$$\Xi(\beta, V, N_{\rm w}, \underline{\lambda}_{\rm guest}) = \sum_{\underline{N}}^{\infty} \prod_{j=1}^{n_{\rm guest}} \prod_{i=1}^{n_{\rm cav}} Q^{\rm EL} W_i \lambda_j^{\sum_{i=1}^{n_{\rm cav}} N_{i,j}} h_{i,j}^{N_{i,j}}$$
(2.48)

Rearranging Expression (2.48) for more clarity in the dependencies of sums and products, we write Expression (2.49).

$$\Xi(\beta, V, N_{\rm w}, \underline{\lambda}_{\rm guest}) = Q^{\rm EL} \sum_{\underline{N}}^{\infty} \prod_{j=1}^{n_{\rm guest}} \lambda_j^{\sum_{k=1}^{n_{\rm cav}} N_{k,j}} \prod_{i=1}^{n_{\rm cav}} W_i h_{i,j}^{N_{i,j}}$$
(2.49)

Finally, the term $\prod_{j=1}^{n_{\text{guest}}} \lambda_j^{\sum_{k=1}^{n_{\text{cav}}} N_{k,j}}$ can be expressed as a product in cavities and guests, as

Expression (2.50) shows.

$$\prod_{j=1}^{n_{\text{guest}}} \lambda_j^{\sum_{i=1}^{n_{\text{cav}}} N_{i,j}} = \prod_{j=1}^{n_{\text{guest}}} \lambda_j^{N_{1,j}} \times \lambda_j^{N_{2,j}} \times \dots \times \lambda_j^{N_{n_{\text{cav}},j}} = \prod_{j=1}^{n_{\text{guests}}} \prod_{i=1}^{n_{\text{cav}}} \lambda_j^{N_{i,j}}$$
(2.50)

Expression (2.49), then, becomes Expression (2.51).

$$\Xi(\beta, V, N_{\rm w}, \underline{\lambda}_{\rm guest}) = Q^{\rm EL} \sum_{\underline{N}}^{\infty} \prod_{i=1}^{n_{\rm guest}} W_i \prod_{j=1}^{n_{\rm guest}} h_{i,j}^{N_{i,j}} \lambda_j^{N_{i,j}}$$
(2.51)

We must take into account that guest molecules are trapped in cavities of different types and that there is only one molecule per cavity at maximum – Assumption (b). Hence, the summations in Equation (2.51) must not reach infinity, but the maximum number of guest molecules in cavity type $i(M_i)$, for the sum of all molecules in each type of cavity cannot be greater than the cavities number itself.

$$\begin{cases} \Xi\left(\beta, V, N_{w}, \underline{\lambda}_{guests}\right) = Q^{EL} \sum_{\underline{N}}^{\infty} \prod_{i=1}^{n_{cav}} W_{i} \prod_{j=1}^{n_{guest}} h_{i,j}^{N_{i,j}} \lambda_{j}^{N_{i,j}} \\ \sum_{j=1}^{n_{guest}} N_{i,j} \leq M_{i} \quad i \in [1, \cdots, n_{cav}] \end{cases}$$

$$(2.52)$$

If we substitute the expression for W_i , we can obtain the expression for Ξ directly from its independent variables.

$$\begin{cases} \Xi = Q^{\text{EL}} \sum_{\underline{N}}^{\infty} \prod_{i=1}^{n_{\text{cav}}} \left[\frac{(v_i N_w)!}{\left(v_i N_w - \sum_{j=1}^{n_{\text{guests}}} N_{i,j} \right)!} \prod_{j=1}^{n_{\text{guests}}} N_{i,j}! \prod_{j=1}^{n_{\text{guests}}} \lambda_j^{N_{i,j}} \lambda_j^{N_{i,j}} \right] \\ \sum_{j=1}^{n_{\text{guest}}} N_{i,j} \le M_i \quad i \in [1, \cdots, n_{\text{cav}}] \end{cases}$$
(2.53)

If we want to respect the constraint imposed in Equation (2.53) we know that the following relation must hold.

$$\sum_{j=1}^{n_{\text{guest}}} N_{i,j} \le M_i \Leftrightarrow N_{i,j} \le M_i$$
(2.54)

Thus, summations in Equation (2.53) can be rewritten. We know that summations of the number of guest molecules of type j within cages of type i from zero to infinity are equivalent to the summations from zero to M_i if both are subject to the constrain in Equation (2.53), as number of molecules larger than M_i are excluded from the sum. Then, we have

$$\begin{cases} \Xi = \mathcal{Q}^{\text{EL}} \sum_{N_{1,1}=0}^{M_1} \sum_{N_{2,1}=0}^{M_2} \cdots \sum_{N_{n_{\text{cav}}}, n_{\text{guest}}}^{n_{\text{cav}}} \prod_{i=1}^{n_{\text{cav}}} \left[\frac{(v_i N_w)!}{(v_i N_w - \sum_{j=1}^{n_{\text{guests}}} N_{i,j})! \prod_{j=1}^{n_{\text{guests}}} N_{i,j}!} \prod_{j=1}^{n_{\text{guests}}} h_{i,j}^{N_{i,j}} \lambda_j^{N_{i,j}} \right] \\ \sum_{j=1}^{n_{\text{guest}}} N_{i,j} \le M_i \quad i \in [1, \cdots, n_{\text{cav}}] \end{cases}$$
(2.55)

The expression above can be further simplified with the aid of the multinomial theorem. According to McQuarrie⁷³, the multinomial theorem states the following:

$$\left(x_{1}+x_{2}+\dots+x_{m}\right)^{n} = \sum_{k_{1}=0}^{n} \sum_{k_{2}=0}^{n} \cdots \sum_{k_{m}}^{n} \binom{n}{k_{1},k_{2},\dots,k_{m}} \prod_{t=1}^{m} x_{t}^{k_{t}}$$
(2.56)

Under the following complementary restriction:

$$k_1 + k_2 + \dots + k_m = n \tag{2.57}$$

If one looks at the semi-grand canonical partition function – Equation (2.55) –, one can see several similarities with the multinomial theorem – Equation (2.56). Firstly, we see that the necessary condition for the validity of the theorem is observed in the combinatorial term from the partition function. $v_i N_w$ represents the number of cavities of type *i* in the clathrate structure and

its equivalent in the general multinomial theorem expression is *n*. The term $\left(v_i N_w - \sum_{j=1}^{n_{guests}} N_{i,j}\right)$

corresponds to k_1 in Equation (2.57) and it represents the cages of type *i* that have not been occupied and $N_{i,j}$ represents the cavities of type *i* occupied by guest *j*. The product of factorial terms goes up to the total number of guests and this means that, for each cavity of type *i*, we have:

$$\left(\nu_{i}N_{w}\right) = \left(\nu_{i}N_{w} - \sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right) + \left(\sum_{j=1}^{n_{\text{guests}}} N_{i,j}\right)$$
(2.58)

This is the equivalent to the following relation, from Equation (2.57):

$$n = k_1 + \sum_{j=2}^{m} k_j$$
(2.59)

The product of $\prod_{j=1}^{n_{\text{guests}}} h_{i,j} \lambda_j^{N_{i,j}}$ is equivalent to the product $\prod_{t=1}^m x_t^{k_t}$. However, it should be

noted that the first term in the combination is related to the empty cavities.

$$k_{1} = \left(\nu_{i} N_{w} - \sum_{j=1}^{n_{guests}} N_{i,j}\right)$$
(2.60)

For the multinomial theorem to be valid, this term needs to be associated with a contribution in the product.

$$\prod_{t=1}^{m} x_{t}^{k_{t}} = \prod_{j=1}^{n_{guests}} h_{i,j}^{N_{i,j}} \lambda_{j}^{N_{i,j}}$$
(2.61)

The contribution of this term in the product is made evident by using a power of 1, not fundamentally changing the product in Equation (2.62). Then, we still have a valid application of the multinomial theorem:

$$\prod_{j=1}^{n_{\text{guests}}} h_{i,j}^{N_{i,j}} \lambda_j^{N_{i,j}} = 1^{\nu_i N_w} \times \prod_{j=1}^{n_{\text{guests}}} h_{i,j}^{N_{i,j}} \lambda_j^{N_{i,j}} = x_1^{k_1} \prod_{t=2}^m x_t^{k_t}$$
(2.62)

From this, we can rewrite Expression (2.55) as a sum of products between activities and partition functions:

$$\Xi = \mathcal{Q}^{\text{EL}} \prod_{i=1}^{n_{\text{cav}}} \left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j \right)^{\nu_i N_w}$$
(2.63)

Then, we have finally arrived at the van der Waals and Platteeuw semi-grand canonical partition function:

$$\Xi(\beta, V, N_{\rm w}, \underline{\lambda}_{\rm guests}) = \exp(-\beta A^{\rm EL}) \prod_{i=1}^{n_{\rm cav}} \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j\right)^{\nu_i N_{\rm w}}$$
(2.64)

2.7. Macroscopic Properties from a Semi-grand Canonical Potential

The partition function expressed earlier in Equation (2.64) can now be used to describe macroscopic thermodynamic variables of the clathrate. The microcanonical partition function is closely related to the entropy of the system. However, other partition functions originate other thermodynamic potentials. The partition functions of common ensembles, like the canonical or the isothermal-isobaric ensembles, originate well-known thermodynamic potentials (Helmholtz energy and Gibbs energy, respectively). Other less common ensembles, like the grand canonical (T,V,μ) , originates less common potentials, like the Landau Potential (-*PV*). In the case of the semigrand canonical partition function, the thermodynamic potential obtained would have a hybrid nature, being close to the Helmholtz energy for the empty lattice and close to the Landau potential for the guests. Hence, we define our potential (Ψ):

$$\Psi(T, V, N_{\rm w}, \underline{\mu}_{\rm guests}) = -k_{\rm B}T\ln\Xi(T, V, N_{\rm w}, \underline{\mu}_{\rm guests})$$
(2.65)

Each of the ensemble transformations we performed earlier to arrive at Expression (2.64) correspond to a Legendre transform of thermodynamic potentials with respect to macroscopic variables. Firstly, we postulated a microcanonical partition function, which means that we could obtain entropy as a function of (E, V, N). The relation between these variables comes from the fundamental thermodynamic relation. In this relation, the independent variables are, commonly,

(S,V,N) and we will follow this paradigm for cohesion with classical thermodynamics literature. Hence, we have the total differential of *E* with respect to the other independent variables:

$$dE = TdS - PdV + \sum_{i=1}^{n_{\text{comp}}} \mu_i dN_i$$
(2.66)

If we rewrite the total differential of *E* we have that:

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,\underline{N}} dS + \left(\frac{\partial E}{\partial V}\right)_{S,\underline{N}} dV + \sum_{i=1}^{n_{\text{comp}}} \left(\frac{\partial E}{\partial N_i}\right)_{S,N_{i\neq j}} dN_i$$
(2.67)

Because of Euler's theorem, we know that the integral expression for these variables can be written as in Equation (2.68):

$$E(S,V,\underline{N}) = TS - PV + \sum_{i=1}^{n_{\text{comp}}} \mu_i N_i$$
(2.68)

The change from the microcanonical to canonical partition function implies the permutation of entropy and temperature as independent variables. The Legendre transform of E that considers this change is the Helmholtz energy. Its integral form is obtained as follows:

$$A = E - \left(\frac{\partial E}{\partial S}\right)_{T,\underline{N}} S \tag{2.69}$$

$$A = E - TS \tag{2.70}$$

For the differential form, we have:

$$dA = dE - TdS - SdT \tag{2.71}$$

$$dA = -SdT - PdV + \sum_{i=1}^{n_{\text{comp}}} \mu_i dN_i$$
(2.72)

Now, if we want to obtain the integral expression of Ψ we have to substitute the number of guest molecules by the chemical potential of guest molecules as independent variables. This leads to the following Legendre transform:

$$\Psi = A - \sum_{i=1}^{n_{\text{guets}}} \left[\left(\frac{\partial A}{\partial N_i} \right)_{T,V,\underline{\mu},N_{i\neq j}} N_i \right]$$
(2.73)

$$\Psi = A - \sum_{i=1}^{n_{\text{guests}}} \mu_i N_i = E - TS - \sum_{i=1}^{n_{\text{guests}}} \mu_i N_i$$
(2.74)

For the differential form, we have:

$$d\Psi = dA - \sum_{i=1}^{n_{\text{guests}}} \mu_i dN_i - \sum_{i=1}^{n_{\text{guests}}} N_i d\mu_i$$
(2.75)

$$d\Psi = -SdT - PdV - \sum_{i=1}^{n_{guest}} N_i d\mu_i + \mu_w dN_w$$
(2.76)

However, the clathrate partition function is based on absolute activities rather than chemical potentials. As we know the definition of absolute activities in terms of chemical potential - Equation (2.44) – we can rewrite Equation (2.75) using more convenient variables.

$$\lambda_{j} = \exp\left(\frac{\mu_{j}}{k_{\rm B}T}\right) \Longrightarrow d\mu_{j} = k_{\rm B}T\ln\lambda_{j}dT + \frac{k_{\rm B}T}{\lambda_{j}}d\lambda_{j}$$
(2.77)

$$d\Psi = -\left(S + \sum_{j=1}^{n_{\text{guest}}} k_{\text{B}}N_{j}\ln\lambda_{j}\right)dT - PdV - \sum_{j=1}^{n_{\text{guest}}} \frac{N_{j}k_{\text{B}}T}{\lambda_{j}}d\lambda_{j} + \mu_{\text{w}}dN_{\text{w}}$$
(2.78)

In its integral form, we have:

$$\Psi = E - TS - \sum_{j=1}^{n_{\text{guests}}} N_j k_{\text{B}} T \ln \lambda_j$$
(2.79)

Because we know the relation of Ψ with the partition function Ξ , we can derive expressions for the entropy and the pressure of the whole clathrate, the chemical potential of host molecules and the number of molecules of guests simply by comparing the expression below to Expression (2.78):

$$d\Psi = \left(\frac{\partial\Psi}{\partial T}\right)_{V,N_{\rm w},\underline{\lambda}} dT + \left(\frac{\partial\Psi}{\partial V}\right)_{T,N_{\rm w},\underline{\lambda}} dV + \left(\frac{\partial\Psi}{\partial N_{\rm w}}\right)_{T,V,\underline{\lambda}} dN_{\rm w} + \sum_{i=j}^{n_{\rm guest}} \left(\frac{\partial\Psi}{\partial\lambda_j}\right)_{T,V,N_{\rm w},\lambda_{i\neq j}} d\lambda_j \quad (2.80)$$

Then, we have that:

$$S = -\left(\frac{\partial\Psi}{\partial T}\right)_{V,N_{\rm w},\underline{\lambda}} - \sum_{j=1}^{n_{\rm guest}} k_{\rm B} N_j \ln\lambda_j$$
(2.81)

$$P = -\left(\frac{\partial\Psi}{\partial V}\right)_{T,N_{\rm w},\underline{\lambda}}$$
(2.82)

$$N_{j} = -\frac{\lambda_{j}}{k_{\rm B}T} \left(\frac{\partial \Psi}{\partial \lambda_{j}}\right)_{T,V,N_{\rm w},\lambda_{i\neq j}}$$
(2.83)

$$\mu_{\rm w} = \left(\frac{\partial \Psi}{\partial N_{\rm w}}\right)_{T,V,\underline{\lambda}} \tag{2.84}$$

One can derive the remaining thermodynamic properties by the mathematical development below. Expression (2.85) represents the chain rule applied to the ratio $\Psi / k_{\rm B}T$.

$$d\left(\frac{\Psi}{k_{\rm B}T}\right) = \frac{1}{k_{\rm B}T}d\Psi - \frac{\Psi}{k_{\rm B}T^2}dT$$
(2.85)

As we know the integral expression for Ψ and its differential form, we can write:

$$d\left(\frac{\Psi}{k_{\rm B}T}\right) = -\frac{S}{k_{\rm B}T}dT - \sum_{j=1}^{n_{\rm guest}}\frac{N_j \ln \lambda_j}{T}dT - \frac{P}{k_{\rm B}T}dV - \sum_{j=1}^{n_{\rm guest}}\frac{N_j}{\lambda_j}d\lambda_j + \frac{\mu_{\rm w}}{k_{\rm B}T}dN_{\rm w} + \frac{E}{k_{\rm B}T^2}dT + \frac{S}{k_{\rm B}T}dT + \sum_{j=1}^{n_{\rm guest}}\frac{N_j \ln \lambda_j}{T}dT$$

$$(2.86)$$

Finally, we have:

$$d\left(\frac{\Psi}{k_{\rm B}T}\right) = -\frac{P}{k_{\rm B}T}dV - \sum_{j=1}^{n_{\rm guest}}\frac{N_j}{\lambda_j}d\lambda_j + \frac{\mu_{\rm w}}{k_{\rm B}T}dN_{\rm w} - \frac{E}{k_{\rm B}T^2}dT$$
(2.87)

The expression above means that we can obtain the internal energy of clathrates by derivation of the ratio $\Psi / k_{\rm B}T$, with respect to temperature.

$$\frac{E}{k_{\rm B}T^2} = -\left[\frac{\partial \left(\Psi / k_{\rm B}T\right)}{\partial T}\right]_{V,\underline{\lambda},N_{\rm w}}$$
(2.88)

Clathrate enthalpy would then be:

$$H = E + PV = -k_{\rm B}T^2 \left[\frac{\partial \left(\Psi / k_{\rm B}T \right)}{\partial T} \right]_{V,\underline{\lambda},N_{\rm w}} - V \left(\frac{\partial \Psi}{\partial V} \right)_{T,N_{\rm w},\underline{\lambda}}$$
(2.89)

Table 1 summarizes the expression for the thermodynamic properties derived here from clathrates semi-grand canonical partition function.

Thermodynamic	Expression
Property	
Entropy	$S = -\left(\frac{\partial \Psi}{\partial T}\right)_{V,N_{\rm w},\underline{\lambda}} - \sum_{j=1}^{n_{\rm guest}} k_{\rm B} N_j \ln \lambda_j$
Pressure	$P = -\left(\frac{\partial \Psi}{\partial V}\right)_{T,N_{\rm w},\underline{\lambda}}$
Number of Guest	$\lambda_{j} \left(\partial \Psi \right)$
Molecules	$N_{j} = -\frac{1}{k_{\mathrm{B}}T} \left(\frac{\partial \lambda_{j}}{\partial \lambda_{j}}\right)_{T,V,N_{\mathrm{w}},\lambda_{i\neq j}}$
Chemical potential of	$u = \left(\frac{\partial \Psi}{\partial \Psi}\right)$
Host Molecules	$\mathcal{P}_{w} \left(\partial N_{w} \right)_{T,V,\underline{\lambda}}$
Internal Energy	$\frac{E}{E} = -\left[\frac{\partial (\Psi / k_{\rm B}T)}{\partial (\Psi / k_{\rm B}T)}\right]$
	$k_{\rm B}T^2$ $\begin{bmatrix} \partial T \end{bmatrix}_{V,\underline{\lambda},N_{\rm w}}$
Enthalpy	$H = E + PV = -k_{\rm B}T^2 \left[\frac{\partial \left(\Psi / k_{\rm B}T\right)}{\partial T}\right]_{V,\underline{\lambda},N_{\rm w}} - V \left(\frac{\partial \Psi}{\partial V}\right)_{T,N_{\rm w},\underline{\lambda}}$

2.8. Macroscopic Properties as Separate Contributions from the Empty Lattice and the Enclathration of Guest Molecules

Ever since the beginning of these derivations, we stated that the empty lattice and the guest molecules grant independent contributions to the partition function by the assumptions of the model. That is evident when we think about the separable Hamiltonian of the system and the partition function of the clathrate, which is a multiplication of several partition functions. Hence, the same degree of separation will be perceived in a macroscopic level, by the thermodynamic

properties derived in the last section. To prove this in a convenient manner, we first show the expression for the logarithm of Ξ .

$$\ln \Xi \left(T, V, N_{\rm w}, \underline{\lambda} \right) = \ln Q^{\rm EL} + \sum_{i=1}^{n_{\rm cav}} v_i N_{\rm w} \ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right)$$
(2.90)

We rewrite this expression using the relation of the canonical partition function to Helmholtz energy for the empty lattice contribution:

$$\ln \Xi \left(T, V, N_{\rm w}, \underline{\lambda} \right) = -\frac{A^{\rm EL}}{k_{\rm B}T} + \sum_{i=1}^{n_{\rm cav}} v_i N_{\rm w} \ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right)$$
(2.91)

Now we will proceed to derive expressions for thermodynamic properties mentioned in the last section directly from the clathrate partition function. However, we will change the order in which they appear, as the reader will notice.

Number of Guest Molecules and Cavity Occupancy

We begin by finding an expression for the number of guest molecules of species *j*. It can be obtained from the differentiation of the partition function with respect to absolute activities, as Equation (2.92) shows.

$$N_{j} = k_{\rm B} T \lambda_{j} \left(\frac{\partial \ln \Xi}{\partial \lambda_{j}} \right)_{T, V, N_{\rm w}, \lambda_{isj}} = \sum_{i=1}^{n_{\rm cav}} \frac{\nu_{i} N_{\rm w} h_{i,j} \lambda_{j}}{\left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_{j} \right)}$$
(2.92)

The number of guest molecules is not a convenient property in the study of clathrates. Instead, cavity occupancies are the common way to take into account the number of guests in the clathrate structure. They are defined as follows:

$$\theta_{i,j} = \frac{N_{i,j}}{v_i N_{\rm w}} \tag{2.93}$$

They represent the relative amount of a guest of type j in cavities of type i and those variables are bracketed between zero and one, according to the van der Waals and Platteeuw assumptions. Given that the number of molecules j can be obtained by the sum of j molecules in all types of cavity, we recall that:

$$N_{j} = \sum_{i=1}^{n_{\text{cav}}} N_{i,j}$$
(2.94)

From Equation (2.92) and Equation (2.94), it can be shown that:

$$N_{i,j} = \frac{v_i N_w h_{i,j} \lambda_j}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j\right)}$$
(2.95)

Substituting the expression for $N_{i,j}$ into Equation (2.93), cavity occupations can be computed from the enclathration partition functions and the activities of guest molecules.

$$\theta_{i,j} = \frac{h_{i,j}\lambda_j}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j}\lambda_j\right)}$$
(2.96)

In several of the derivations in this section, we deal with expressions like the one below:

$$\frac{\sum_{i=1}^{n_{\text{guests}}} \lambda_j \left(\frac{\partial h_{i,j}}{\partial \xi}\right)}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j\right)}$$
(2.97)

In which ξ represents any thermodynamic variable. To express Equation (2.97) in terms of cavity occupation, we use the following algebraic manipulation:

$$\frac{\sum_{i=1}^{n_{\text{guests}}} \lambda_j \left(\frac{\partial h_{i,j}}{\partial \xi}\right) \times \frac{h_{i,j}}{h_{i,j}}}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j\right)} = \frac{\sum_{i=1}^{n_{\text{guests}}} \lambda_j h_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial \xi}\right)}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j\right)} = \sum_{i=1}^{n_{\text{guests}}} \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial \xi}\right)$$
(2.98)

Entropy

For the entropy, the differentiation of the partition function with respect to temperature plus the sum of logarithm of activities leads to:

$$S = k_{\rm B} \ln \Xi + k_{\rm B} T \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V, N_{\rm w}, \underline{\lambda}} = -\left(\frac{\partial A^{\rm EL}}{\partial T} \right) + k_{\rm B} \sum_{i=1}^{n_{\rm cav}} v_i N_{\rm w} \left\{ \ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right) + T \left[\frac{\sum_{i=1}^{n_{\rm guests}} \lambda_j \left(\frac{\partial h_{i,j}}{\partial T} \right)_{V, \lambda_{i\neq j}, N_{\rm w}}}{\left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right)} \right] \right\} - \sum_{j=1}^{n_{\rm guest}} k_{\rm B} N_j \ln \lambda_j$$

$$(2.99)$$

Using Equation (2.98), we arrive at:

$$S = S^{\text{EL}} + k_{\text{B}} \sum_{i=1}^{n_{\text{cav}}} \nu_i N_{\text{w}} \left\{ \ln \left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j \right) + \sum_{i=1}^{n_{\text{guests}}} \theta_{i,j} \left[T \left(\frac{\partial \ln h_{i,j}}{\partial T} \right)_{V,\lambda_{i \neq j},N_{\text{w}}} + \ln \lambda_j \right] \right\}$$
(2.100)

Pressure

For the pressure, the substitution of Equation (2.82) leads to:

$$P = k_{\rm B} T \left(\frac{\partial \ln \Xi}{\partial V} \right)_{T, N_{\rm w}, \underline{\lambda}} = -\left(\frac{\partial A^{\rm EL}}{\partial V} \right)_{T, N_{\rm w}} + k_{\rm B} T \sum_{i=1}^{n_{\rm cav}} v_i N_{\rm w} \frac{\sum_{i=1}^{n_{\rm cav}} \lambda_j \left(\frac{\partial h_{i,j}}{\partial V} \right)_{T, \lambda_{isj}, N_{\rm w}}}{1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j}$$
(2.101)

In addition, the Equation (2.98) simplifies Equation (2.101) to:

$$P = P^{\rm EL} + N_{\rm w} k_{\rm B} T \sum_{i=1}^{n_{\rm cav}} \sum_{i=1}^{n_{\rm suests}} v_i \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial V} \right)_{T,\lambda_{i\neq j},N_{\rm w}}$$
(2.102)

Chemical Potential of Host Molecules

For the chemical potential of the host molecules, we have:

$$\mu_{\rm w} = k_{\rm B} T \left(\frac{\partial \ln \Xi}{\partial N_{\rm w}} \right)_{T,V,\underline{\lambda}} = \left(\frac{\partial A^{\rm EL}}{\partial N_{\rm w}} \right)_{T,V,\underline{\lambda}} - k_{\rm B} T \sum_{i=1}^{n_{\rm cav}} \nu_i \left[\ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right) + N_{\rm w} \frac{\sum_{i=1}^{n_{\rm guests}} \lambda_j \left(\frac{\partial h_{i,j}}{\partial N_{\rm w}} \right)_{T,V,\underline{\lambda}}}{\left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right)} \right]$$
(2.103)

In addition, Equation (2.98) simplifies Equation (2.103) into Equation (2.104).

$$\mu_{\rm w} = \left(\frac{\partial A^{\rm EL}}{\partial N_{\rm w}}\right)_{T,V,\underline{\lambda}} - k_{\rm B}T \sum_{i=1}^{n_{\rm cav}} \nu_i \left[\ln\left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j}\lambda_j\right) + N_{\rm w} \sum_{i=1}^{n_{\rm guests}} \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial N_{\rm w}}\right)_{T,V,\underline{\lambda}}\right]$$
(2.104)

The derivative of the Helmholtz free energy for the empty lattice is the chemical potential of water in the empty hydrate. Therefore, we arrive at an analogous expression of the famed van der Waals and Platteeuw chemical potential difference between water in the empty lattice and in the clathrate with the added contribution of $h_{i,j}(V, N_w)$.

$$\mu_{\rm w}^{\rm H} = \mu_{\rm w}^{\rm EL} - k_{\rm B} T \sum_{i=1}^{n_{\rm cav}} \nu_i \left[\ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right) + N_{\rm w} \sum_{i=1}^{n_{\rm guests}} \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial N_{\rm w}} \right)_{T,V,\underline{\lambda}} \right]$$
(2.105)

Internal Energy

For the internal energy, we have the following.

$$E = -k_{\rm B}T^{2} \left[\frac{\partial \left(\Psi / k_{\rm B}T \right)}{\partial T} \right]_{V,\underline{\lambda},N_{\rm w}} = k_{\rm B}T^{2} \left[\frac{\partial \left(\ln \Xi \right)}{\partial T} \right]_{V,\underline{\lambda},N_{\rm w}} = k_{\rm B}T^{2} \left[\frac{\partial \left(-A^{\rm EL} / k_{\rm B}T \right)}{\partial T} \right]_{V,N_{\rm w}} + k_{\rm B}T^{2} \sum_{i=1}^{n_{\rm cav}} \nu_{i}N_{\rm w} \frac{\sum_{i=1}^{n_{\rm guests}} \lambda_{j} \left(\frac{\partial h_{i,j}}{\partial T} \right)_{V,\lambda_{isj},N_{\rm w}}}{\left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j}\lambda_{j} \right)}$$
(2.106)

From classical thermodynamics, we know that we can obtain the internal energy from a derivative of the Helmholtz energy with respect to temperature. Hence:

$$E = E^{\text{EL}} + k_{\text{B}}T^{2}\sum_{i=1}^{n_{\text{cav}}} \nu_{i}N_{\text{w}} \frac{\sum_{i=1}^{n_{\text{guest}}} \lambda_{j} \left(\frac{\partial h_{i,j}}{\partial T}\right)_{V,\lambda_{i\neq j},N_{\text{w}}}}{\left(1 + \sum_{i=1}^{n_{\text{guest}}} h_{i,j}\lambda_{j}\right)}$$
(2.107)

Using Equation (2.98), we arrive at Expression (2.108).

$$E = E^{\mathrm{EL}} + N_{\mathrm{w}} k_{\mathrm{B}} T^{2} \sum_{i=1}^{n_{\mathrm{cav}}} \sum_{i=1}^{n_{\mathrm{uest}}} \nu_{i} \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial T} \right)_{V,\lambda_{i\neq j},N_{\mathrm{w}}}$$
(2.108)

Enthalpy

The hydrate enthalpy is, then, obtained by substituting the expression for pressure and internal energy, resulting in Equation (2.110).

$$H = E^{\mathrm{EL}} + P^{\mathrm{EL}}V + N_{\mathrm{w}}k_{\mathrm{B}}T\sum_{i=1}^{n_{\mathrm{cav}}}\sum_{i=1}^{n_{\mathrm{guest}}}v_{i}\theta_{i,j}\left[T\left(\frac{\partial\ln h_{i,j}}{\partial T}\right)_{V,\lambda_{i\neq j},N_{\mathrm{w}}} + V\left(\frac{\partial\ln h_{i,j}}{\partial V}\right)_{T,\lambda_{i\neq j},N_{\mathrm{w}}}\right]$$
(2.109)
$$H = H^{\mathrm{EL}} + N_{\mathrm{w}}k_{\mathrm{B}}T\sum_{i=1}^{n_{\mathrm{cav}}}\sum_{i=1}^{n_{\mathrm{guest}}}v_{i}\theta_{i,j}\left[T\left(\frac{\partial\ln h_{i,j}}{\partial T}\right)_{V,\lambda_{i\neq j},N_{\mathrm{w}}} + V\left(\frac{\partial\ln h_{i,j}}{\partial V}\right)_{T,\lambda_{i\neq j},N_{\mathrm{w}}}\right]$$
(2.110)

All clathrate properties split into their empty lattice and enclathration contributions are summarized in Table 2.

Property	Empty Lattice Contribution	Enclathration + Guest Molecules Contributions
Number of Guest Molecules (N_j)	None	$\sum_{i=1}^{n_{\text{cav}}} \frac{\nu_i N_{\text{w}} h_{i,j} \lambda_j}{\left(1 + \sum_{i=1}^{n_{\text{guests}}} h_{i,j} \lambda_j\right)}$
Cage Occupatio n Fraction $\left(\theta_{i,j}\right)$	None	$\frac{h_{i,j}\lambda_j}{\left(1+\sum_{i=1}^{n_{\text{guests}}}h_{i,j}\lambda_j\right)}$
Entropy (S^{H})	$S^{\scriptscriptstyle \mathrm{EL}}$	$\left k_{\rm B} \sum_{i=1}^{n_{\rm cav}} \nu_i N_{\rm w} \left\{ \ln \left(1 + \sum_{i=1}^{n_{\rm guests}} h_{i,j} \lambda_j \right) + \sum_{i=1}^{n_{\rm guests}} \theta_{i,j} \left[T \left(\frac{\partial \ln h_{i,j}}{\partial T} \right)_{V,\lambda_{i\neq j},N_{\rm w}} + \ln \lambda_j \right] \right\}$
$\begin{array}{c} \text{Pressure} \\ \left(P^{\text{H}} \right) \end{array}$	P^{EL}	$N_{\rm w} k_{\rm B} T \sum_{i=1}^{n_{\rm cav}} \sum_{i=1}^{n_{\rm guest}} \nu_i \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial V} \right)_{T,\lambda_{i\neq j},N_{\rm w}}$
Chemical Potential of Host Molecules $\left(\mu_{w}^{H}\right)$	$\mu_{ m w}^{ m EL}$	$-k_{\rm B}T\sum_{i=1}^{n_{\rm cav}} \nu_i \left[\ln\left(1 + \sum_{i=1}^{n_{\rm guest}} h_{i,j}\lambda_j\right) + N_{\rm w}\sum_{i=1}^{n_{\rm guest}} \theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial N_{\rm w}}\right)_{T,V,\underline{\lambda}} \right]$
Internal Energy (E^{H})	$E^{ m EL}$	$N_{\rm w}k_{\rm B}T^2\sum_{i=1}^{n_{\rm cav}}\sum_{i=1}^{n_{\rm guest}}\nu_i\theta_{i,j}\left(\frac{\partial\ln h_{i,j}}{\partial T}\right)_{V,\lambda_{i\neq j},N_{\rm w}}$
Enthalpy (H^{H})	$H^{ m EL}$	$N_{\rm w}k_{\rm B}T\sum_{i=1}^{n_{\rm cav}}\sum_{i=1}^{n_{\rm guest}}\nu_{i}\theta_{i,j}\left[T\left(\frac{\partial\ln h_{i,j}}{\partial T}\right)_{V,\lambda_{i\neq j},N_{\rm w}}+V\left(\frac{\partial\ln h_{i,j}}{\partial V}\right)_{T,\lambda_{i\neq j},N_{\rm w}}\right]$

Table 2 – Properties of clathrates from the empty lattice and enclathration contributions.

2.9. Comments on the Enclathration Partition Function

From Table 2 we see the importance of the enclathration partition function on the determination of clathrate properties. Here, we address some of its features. Firstly, if we go back to the discussion on the Hamiltonian of the system, we see that $h_{i,j}$ comes from the Hamiltonian of enclathration of guest molecules and the number of microstates in which the guest molecules can be within the cavity. We rewrite its definition below:

$$h_{i,j}(T,V,N_{\rm w}) = \sum_{q=1}^{\infty} \Omega_{i,j,q} \exp\left(-\frac{\mathcal{H}_{i,j,q}^{\rm enc}}{k_{\rm B}T}\right)$$
(2.111)

However, knowing that we can separate the Hamiltonian and the number of states once again in its internal molecular contributions and the translation of molecules, we have:

$$\mathcal{H}_{i,j,q}^{\text{enc}} = \mathcal{H}_{j,q}^{\text{int}} + \mathcal{H}_{i,j,q}^{\text{trans}}$$
(2.112)

The translational Hamiltonian is, again, separable into kinetic and potential energy. Therefore, we have:

$$\mathcal{H}_{i,j,q}^{\text{enc}} = \mathcal{H}_{j,q}^{\text{int}} + \frac{p_q^2}{2m_j} + U_{i,j,q}^{\text{enc}} \left(r_q, r_{\text{cav},i}, N_w, V \right)$$
(2.113)

The first two terms in the right-hand side are equivalent to the Hamiltonian of an ideal gas molecule:

$$\mathcal{H}_{i,j,q}^{\text{enc}} = \mathcal{H}_{j,q}^{\text{IG}} + U_{i,j,q}^{\text{enc}} \left(r_q, r_{\text{cav},i}, N_{\text{w}}, V \right)$$
(2.114)

To obtain an expression for the partition function, it is convenient to use the statistical mechanics on the continuous scale for the classical degrees of freedom, thus integrating throughout all possible values of momentum and position and all intramolecular degrees of freedom (q).

$$Q(N,V,\beta) = \int_{-\infty}^{+\infty} \Omega(N,V,E) \exp(-\beta E) dE$$
(2.115)

The substitution of a general expression for the microcanonical partition function of an *N*-body system would lead to the following expression⁷³:

$$Q(N,V,\beta) = \frac{1}{N! h_{Planck}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(\mathcal{H} - E) \exp(-\beta E) d\underline{r} d\underline{p} d\underline{q} dE$$
(2.116)

In this expression *s* is the number of degrees of freedom per particle. This expression would be equivalent to Equation (2.40), which is the partition function for the $(N_w + N_{guest})$ -body clathrate system. We already know from Section 2.4 that the combinatorial term (*W*) deals with two characteristics of the clathrate system: it considers the indistinguishability of the guest particles and it accounts for Assumption (b). Therefore, it splits the $(N_w + N_{guest})$ -body partition

function in space and we only need to deal with the configurational integral of one guest molecule within a cavity $(h_{i,j})$. Thus, the integration for the <u>r</u> coordinates is confined within the volume of a cavity and we have:

$$h_{i,j}(T,V,N_{\rm w}) = \frac{1}{h_{Planck}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta\left(\mathcal{H}_{j,q}^{\rm IG} + U_{i,j,q}^{\rm enc} - E^{\rm enc}\right) \exp\left(-\beta E^{\rm enc}\right) d\underline{r} d\underline{p} d\underline{q} dE \qquad (2.117)$$

The integral in internal energy of the delta function works in the same way as the summations to arrive at a canonical partition function from a microcanonical one. Hence, we have:

$$h_{i,j}(T,V,N_{\rm w}) = \frac{1}{h_{Planck}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left(-\beta \mathcal{H}_{j,q}^{\rm IG} - \beta U_{i,j,q}^{\rm enc}\right) d\underline{r} d\underline{p} d\underline{q}$$
(2.118)

The integration on all intramolecular degrees of freedom and the momentum coordinates yields the one molecule ideal gas partition function of a molecule of type *j* divided by the volume (Φ_j) .

$$h_{i,j}(T,V,N_{\rm w}) = \Phi_j(T) \int_{V_{\rm cav,i}} \exp(-\beta U_{i,j,q}^{\rm enc}) d\underline{r}$$
(2.119)

In which:

$$\Phi_{j} = \left(\frac{2\pi m_{j} k_{\rm B} T}{h_{Planck}^{2}}\right)^{3/2} Q_{j}^{\rm IG, rotational} Q_{j}^{\rm IG, vibrational} = \frac{Q_{j}^{\rm IG, translational}}{V} Q_{j}^{\rm IG, rotational} Q_{j}^{\rm IG, vibrational}$$
(2.120)

Finally, we need to address the so-called configurational integral, the integral term in Equation (2.120). If we consider the potential function, we see that it depends only on the relative position of the particle, having the cavity center as reference. All those observations simplify Equation (2.119) to:

$$h_{i,j}(V_{\text{cav}},\beta) = \Phi_j(T) \int_{0}^{r_{\text{cav},i}} \exp\left[-\beta w_j(r)\right] 4\pi r^2 dr \qquad (2.121)$$

2.10. Introduction of the Langmuir Constants

In order to have a coupling between several models, such as fluid phase equations of state, and the van der Waals and Platteeuw model, it is very convenient to describe guest molecules by their fugacity, instead of their absolute activity. Here, we show a mathematical derivation to the so-called Langmuir constants and we show their relation to the guest-cavity interaction potential. First, the absolute activity is defined.

$$\lambda_j(T,P) = \exp\left[\frac{\mu_j(T,P)}{k_{\rm B}T}\right]$$
(2.122)

We can introduce the chemical potential of component *j* in a mixture of ideal gases (μ_j^{IG}) and the chemical potential of component *j* as a pure ideal gas (PIG) into Equation (2.122).

$$\lambda_{j}(T,P) = \exp\left[\frac{\mu_{j}(T,P)}{k_{B}T} - \frac{\mu_{j}^{IG}(T,P)}{k_{B}T}\right] \times \exp\left[\frac{\mu_{j}^{IG}(T,P)}{k_{B}T} - \frac{\mu_{j}^{PIG}(T,P)}{k_{B}T}\right] \exp\left[\frac{\mu_{j}^{PIG}(T,P)}{k_{B}T}\right]$$
(2.123)

The guest molecules within the clathrate can be described from an ideal gas reference. We see that the first exponential term would be the product of the fugacity coefficient $(\hat{\phi}_j^{\text{H}})$ and the second exponential term would be the mole fraction of component *j* in the clathrate phase (x_j^{H}) .

$$\lambda_{j}(T,P) = \hat{\phi}_{j}^{\mathrm{H}}(T,P) x_{j}^{\mathrm{H}} \exp\left[\frac{\mu_{j}^{\mathrm{PIG}}(T,P)}{k_{\mathrm{B}}T}\right]$$
(2.124)

The chemical potential of the ideal gas can be written using its canonical partition function. According to McQuarrie⁷³, we have that:

$$\mu_{j}^{\text{PIG}}(T,P) = k_{\text{B}}T\ln P - k_{\text{B}}T\ln\left[k_{\text{B}}T\Phi_{j}(T)\right]$$
(2.125)

Substitution of this expression in Equation (2.124) yields:

$$\lambda_{j}(T,P) = \hat{\phi}_{j}^{\mathrm{H}}(T,P) x_{j}^{\mathrm{H}} \exp\left\{\ln P - \ln\left[k_{\mathrm{B}}T\Phi_{j}(T)\right]\right\}$$
(2.126)

Then, we end up with the following expression:

$$\lambda_j = \frac{\hat{\phi}_j^{\mathrm{H}} x_j^{\mathrm{H}} P^{\mathrm{H}}}{k_{\mathrm{B}} T \Phi_j(T)}$$
(2.127)

The numerator on the right-hand side would be the fugacity of species j in the clathrate phase.

$$\lambda_j = \frac{\hat{f}_j^{\rm H}}{k_{\rm B}T\Phi_j(T)} \tag{2.128}$$

If we substitute this expression for the absolute activity of component j in the definition of the cavity occupancies – Equation (2.96) – we would get:

$$\theta_{i,j} = \frac{\frac{h_{i,j}\hat{f}_{j}^{\mathrm{H}}}{k_{\mathrm{B}}T\Phi_{j}(T)}}{\left(1 + \sum_{j=1}^{n_{\mathrm{guests}}} \frac{h_{i,j}\hat{f}_{j}^{\mathrm{H}}}{k_{\mathrm{B}}T\Phi_{j}(T)}\right)}$$
(2.129)

Equation (2.129) is similar to the Langmuir adsorption isotherm, expressed below:

$$\theta_{i,j} = \frac{C_{i,j}P_j}{\left(1 + \sum_{j=1}^{n_{guests}} C_{i,j}P_j\right)}$$
(2.130)

In which θ_j is the occupation of adsorption sites, P_j is the partial pressure of component *j* in the fluid phase and C_j is the so-called Langmuir constant. By inspection of Equations (2.129) and (2.130), we can define an analogous Langmuir constant that has the following expression:

$$C_{i,j} = \frac{h_{i,j}}{k_{\rm B}T\Phi_j(T)}$$
(2.131)

Substituting the expression for $h_{i,j}$ (Equation 2.122), we have:

$$C_{i,j} = \frac{4\pi}{k_{\rm B}T} \int_{0}^{r_{\rm cav,i}} \exp\left[-\beta w_j(r)\right] r^2 dr$$
(2.132)

Moreover, we get the following expression for cavity occupancy:

$$\theta_{i,j} = \frac{C_{i,j}\hat{f}_{j}^{\mathrm{H}}}{\left(1 + \sum_{i=1}^{n_{\mathrm{guests}}} C_{i,j}\hat{f}_{j}^{\mathrm{H}}\right)}$$
(2.133)

If we want to tackle thermodynamic equilibrium problems and determine the conditions at which clathrates can form, we need to solve a system of equilibrium equations involving several phases. If the system is at equilibrium, the fugacity of guest molecules is equal in the hydrate phase and in other fluid phases where it might be present. Hence, it is common to substitute the fugacity of component *j* in the hydrate phase by the fugacity of this very component in a fluid phase and the equality of fugacities for these components disappears from the equilibrium equations. The fugacity of the gas phase can be easily obtained from a regular equation of state and if we also know an expression for the Langmuir constant, we can determine clathrate cage occupancies in a fixed temperature, pressure, and fluid phase composition. From Expression (2.128) we also know that:

$$\lambda_{j} = \frac{\hat{f}_{j}^{H}}{k_{B}T\Phi_{j}(T)} = \hat{f}_{j}^{H}\frac{4\pi}{k_{B}T}\frac{1}{h_{i,j}}\int_{0}^{r_{cav,j}} \exp\left[-\beta w_{j}(r)\right]r^{2}dr$$
(2.134)

Therefore, we have the equality of the fugacity-Langmuir constant and the activitypartition function products, as below.

$$h_{i,j}\lambda_j = \hat{f}_j^{\mathrm{H}}C_{i,j} \tag{2.135}$$

Mathematical manipulation shows that:

$$\sum_{j=1}^{n_{guest}} h_{i,j} \lambda_j + 1 = \frac{1}{1 - \sum_{i=1}^{n_{cav}} \theta_{i,j}}$$
(2.136)

Using Expression (2.135) and Expression (2.136), we can express the thermodynamic properties in a more convenient way, as we will see in following chapter.

3. Methodology

3.1. Deriving the Enthalpy of Dissociation from van der Waals and Platteeuw model

In the last chapter, the van der Waals and Platteeuw model was thoroughly explained. Here, we will use it in order to obtain an expression that can deal with the energetic aspects of gas hydrate formation. As mentioned in the Introduction chapter, 0the modeling of such aspects is of great importance and the van der Waals and Platteeuw model potentialities for these applications have been overlooked by hydrate literature.

In the last Chapter, we derived general expression for gas hydrate properties. Here, we will assume a partition function $h_{i,j}$ that is independent of the number of host molecules and the volume of the clathrate. That is the current approach in hydrate literature. The potential function will be further discussed in the next section. The following manipulations and results are reported in Medeiros et al, 2018⁷⁴.

From Equation (2.108) for hydrate internal energy, we have that:

$$\frac{E^{\mathrm{H}} - E^{\mathrm{EL}}}{N_{\mathrm{w}}k_{\mathrm{B}}T^{2}} = \sum_{j=1}^{n_{\mathrm{guest}}} \sum_{i=1}^{n_{\mathrm{cage}}} \nu_{i}\theta_{i,j} \left(\frac{\partial \ln h_{i,j}}{\partial T}\right)_{V}$$
(3.1)

If we use Langmuir constants introduced in the last section, we obtain the following:

$$C_{i,j} = \frac{1}{k_{\rm B}T} \frac{h_{i,j}}{\Phi_j}$$
(3.2)

Since Φ_j represents the partition function of an ideal gas without the volume term – Equation (2.120) – and we also know that $h_{i,j}$ has the same term – Equation (2.121) – we have that:

$$h_{i,j} = \frac{C_{i,j} k_{\rm B} T}{V} Q_j^{\rm IG}$$
(3.3)

Applying the derivative of the logarithm to the aforementioned h_{ij} expression, one obtains:

$$\left(\frac{\partial \ln h_{i,j}}{\partial T}\right)_{V,N_{w}} = \frac{E_{j}^{IG}}{N_{j}k_{B}T^{2}} + \left[\frac{\partial}{\partial T}\ln\left(\frac{C_{i,j}k_{B}T}{V}\right)\right]_{V}$$
(3.4)

Meaning that Equation (3.1) can be rewritten and a new internal energy term appears:

$$\frac{E^{\mathrm{H}} - E^{\mathrm{EL}} - \sum_{j=1}^{n_{\mathrm{guest}}} N_j \overline{E}_j^{\mathrm{IG}}}{N_{\mathrm{w}} k_{\mathrm{B}} T^2} = \sum_{j=1}^{n_{\mathrm{guest}}} \sum_{i=1}^{n_{\mathrm{cage}}} \nu_i \theta_{i,j} \frac{\partial}{\partial T} \Big[\ln \big(C_{i,j} k_{\mathrm{B}} T \big) \Big]_{V,N_{\mathrm{w}}}$$
(3.5)

This means that the term on the right-hand side of Equation (3.5) is the difference between hydrate internal energy and its two references: the hypothetical empty lattice, as a reference for water, and the ideal gas, as a reference for the guest molecules. The difference in internal energy can once again be rewritten as a difference in enthalpy if an extra term is added to the right-hand side, having in mind that hydrate and empty lattice have the same volume and pressure and that $h_{i,j}$ is not a function of hydrate volume or number of water molecules.

$$\frac{H^{\mathrm{H}} - H^{\mathrm{EL}} - \sum_{j=1}^{n_{\mathrm{guest}}} N_{j} \overline{H}_{j}^{\mathrm{IG}}}{N_{\mathrm{w}} k_{\mathrm{B}} T^{2}} = \sum_{j=1}^{n_{\mathrm{guest}}} \sum_{i=1}^{n_{\mathrm{cage}}} \nu_{i} \theta_{i,j} \frac{\partial}{\partial T} \Big[\ln \Big(C_{i,j} k_{\mathrm{B}} T \Big) \Big]_{V,N_{\mathrm{w}}} - \frac{P \overline{V}^{\mathrm{IG}}}{N_{\mathrm{w}} k_{B} T^{2}} \sum_{j=1}^{n_{\mathrm{guest}}} N_{j}$$
(3.6)

The enthalpy of dissociation measured in calorimetric experiments accounts for the transition from hydrate phase to water and gas phase. If we neglect gas solubility in the liquid phase, we can express the heat of dissociation as in Equation (3.7), in which x_i^{H} represents the mole fraction of component *i* in the hydrate phase, $\overline{H}_w^{\text{PW}}$ represents the molar enthalpy of pure water and $\overline{H}_j^{\text{G}}$ stands for the partial molar enthalpy of component *j* in the gas phase.

$$\Delta \overline{H}_{\text{diss}} = x_{w}^{\text{H}} \overline{H}_{w}^{\text{PW}} + \sum_{j=1}^{n_{\text{guest}}} x_{j}^{\text{H}} \overline{H}_{j}^{\text{G}} - \overline{H}^{\text{H}}$$
(3.7)

Hence, in order to make it compatible with the expression derived from Statistical Thermodynamics – Equation (3.6) – we need to add and subtract the molar enthalpy of the empty lattice. Ultimately, the expression becomes:

$$\Delta \bar{H}_{\text{diss}} = \sum_{j=1}^{n_{\text{guest}}} x_j^{\text{H}} \bar{H}_j^{\text{R}} + RT \sum_{j=1}^{n_{\text{guest}}} x_j^{\text{H}} - x_{\text{w}}^{\text{H}} \Delta \bar{H}_{\text{w}}^{\text{EL-PW}} - x_{\text{w}}^{\text{H}} RT^2 \sum_{j=1}^{n_{\text{guest}}} \sum_{i=1}^{n_{\text{cage}}} \nu_i \theta_{i,j} \left[\frac{\partial}{\partial T} \ln \left(C_{i,j} k_{\text{B}} T \right) \right]_{V, N_{\text{w}}}$$
(3.8)

This expression is analogous to the ones obtained by Avlonitis⁷⁵ and Jäger *et al.*⁷⁶, being the only difference the fact that the former derived it from a derivative of fugacities and the later derived it from expressions for hydrate entropy and Gibbs energy.

3.2. Thermodynamic Modeling

3.2.1. Equilibrium Criteria

Equilibrium criteria used in this work for phase equilibrium calculations was the equality of chemical potentials as follows.

$$\Delta \mu_{\rm w}^{\rm H-EL} + \Delta \mu_{\rm w}^{\rm EL-PW} = 0 \tag{3.9}$$

In Equation (3.9), $\Delta \mu_{w}^{\text{EL-PW}}$ stands for the chemical potential difference between pure water and the water in the empty lattice phase and $\Delta \mu_{w}^{\text{H-EL}}$ represents the chemical potential difference between water in the empty lattice and water in the hydrate phase. We used this criteria directly to formulate the objective function for our parameter estimation methodology, i.e. without the use of an iterative phase equilibrium algorithm as it was done by Parrish and Prasunitz⁷⁷. The objective function will be further explained in Section 2.3 and details on the calculation of each potential difference will be addressed in the remainder of this section. One should have in mind that two important assumptions were made: (i) solubility of methane and carbon dioxide in the water-rich liquid phase was neglected; (ii) hydrate volume is independent of the guest and its dependency on pressure and temperature is considered the same for methane, carbon dioxide and methane + carbon dioxide hydrates.

3.2.2. Chemical potential difference between water and the empty lattice

Chemical potential difference between pure water and the empty lattice was calculated using the following equation.

$$\frac{\Delta\mu_{\rm w}^{\rm EL-PW}\left(T,P\right)}{RT} = \frac{\Delta\mu_{\rm w}^{\rm EL-PW}\left(T_{0},P_{0}\right)}{RT_{0}} - \int_{T_{0}}^{T} \frac{\Delta\overline{H}^{\rm EL-PW}}{RT^{2}} dT + \int_{P_{0}}^{P} \frac{\Delta\overline{V}^{\rm EL-PW}}{RT} dP$$
(3.10)

In which $\Delta \mu_0^{\text{EL-PW}}$ is a parameter, $\Delta \overline{H}^{\text{EL-PW}}$ is expanded as in Equation (3.11) and $\Delta \overline{V}^{\text{EL-PW}}$ is calculated by the difference of empty lattice and pure water molar volumes, according to the correlations presented in this section.

$$\Delta \overline{H}^{\text{EL-PW}}(T) = \Delta \overline{H}_0^{\text{EL-PW}} + \Delta C p_0^{\text{EL-PW}}(T - T_0) + \Delta B_0^{\text{EL-PW}}\left(\frac{T^2}{2} - \frac{T_0^2}{2}\right)$$
(3.11)

The liquid water volume was calculated from Equation (3.12). We generated this correlation based on Hilbert *et al.*⁷⁸ and Lide⁷⁹ experimental data.

$$\overline{V}^{\text{LW}} / (\text{m}^{3}\text{mol}^{-1}) = \left[1.00453 \times 10^{-10} (T/\text{K})^{2} - 5.71157 \times 10^{-8} (T/\text{K}) + 2.61517 \times 10^{-5} \right] \times \exp\left[3.30859 \times 10^{-10} (P/\text{Pa} - 101325.) \right]$$
(3.12)

For ice volume, we used the correlation proposed by Klauda and Sandler¹¹. We proposed an empty lattice volume correlation by combining unit cell parameter information from Shpakov *et al.*⁸⁰ and isothermal compression data from Klapproth *et al.*⁸¹, which yielded the following expression.

$$\overline{V}^{\text{EL}} / (\text{m}^{3}\text{mol}^{-1}) = \left[11.8 + 5.39 \times 10^{-5} (T/\text{K}) + 1.78 \times 10^{-6} (T/\text{K})^{2} \right]^{3} \left(\frac{10^{-30} N_{\text{AV}}}{46} \right) \times \exp\left[-1.098 \times 10^{-10} \times (P/\text{Pa} - 101325) \right]$$
(3.13)

The enthalpy difference between the empty lattice and liquid water was one of the parameters we estimated and the difference in heat capacity used was the expression proposed by John, Papadopoulos and Holder¹⁴. Reference temperature and pressure are 273.15 K and 101,325 Pa, respectively.

3.2.3. Chemical potential difference between water in hydrate and water in the empty lattice.

The chemical potential difference between water in hydrate and water in the empty lattice is represented in Equation (3.14).

$$\Delta \mu_{\rm w}^{\rm H-EL}\left(T, P, \underline{x}^{\rm V}\right) = RT \ln \left\{ \prod_{j} \left[\left(1 - \sum_{i} \left(\theta_{i,j}\right)\right)^{\nu_{j}} \right] \right\}$$
(3.14)

Cage occupancies were calculated according to Equation (3.15).

$$\theta_{i,j}\left(T,P,\underline{x}^{\mathrm{V}}\right) = \frac{C_{i,j}\left(T\right)f_{i}\left(T,P,\underline{x}^{\mathrm{V}}\right)}{\left\{\sum_{k}\left[C_{k,j}\left(T\right)f_{k}\left(T,P,\underline{x}^{\mathrm{V}}\right)\right]+1\right\}}$$
(3.15)

The Langmuir constant was obtained from the integration of a radially symmetrical potential within a single hydrate cavity. We tested the Kihara Potential¹³ and its natural limiting case for zero hard core radius, the Lennard-Jones 12-6 potential¹³, proved to be more appropriate. This change will be further discussed in the Results section. Potential parameters used here are mean values between guest *i* potential parameters and water potential parameters. They were obtained as follows. The superscript "hyd" will be henceforth omitted for simplicity.

$$a_i^{\rm hyd} = \frac{a_{ii} + a_{\rm ww}}{2}$$
(3.16)

$$\sigma_i^{\text{hyd}} = \frac{\sigma_{ii} + \sigma_{\text{ww}}}{2}$$
(3.17)

$$\varepsilon_i^{\text{hyd}} = \left(\varepsilon_{ii}\varepsilon_{\text{ww}}\right)^{1/2} \tag{3.18}$$

The cavity radius used here was the same as in John, Papadopoulos and Holder's work¹⁴. However, we did not include multiple water shells in our work as the mentioned authors did. We did not do so because the determination of water coordination and shell radii is somewhat arbitrary and the inclusion of such shells would not improve accuracy, for we fitted potential parameters to macroscopic properties. Coordination numbers used for the only shell were obtained in Sloan and Koh's book³.

The vapor phase fugacity was modelled by the Peng-Robinson⁸² cubic equation of state, contemplating mixtures using the classical mixing and combining rules with binary interaction parameters for the attractive parameter (*a*). Experimental data used here for carbon dioxide simple hydrates included only points at pressures and temperatures below the second quadruple point of

(2 1 0)
water + carbon dioxide system with water in excess $(4.499 \text{ MPa and } 283 \text{ K})^3$. Therefore, the only liquid phase present in the parameter estimation step is pure water.

3.3. Parameter Estimation and Experimental Data

3.3.1. Parameter Regression Methodology

The parameters that are usually estimated in hydrate literature are those of the Langmuir constant and the hydrate formation parameters ($\Delta \mu_0^{\text{EL-PW}}$, $\Delta \overline{H}_0^{\text{EL-LW}}$ and $\Delta C p_0^{\text{EL-PW}}$). In this work we follow the same guidelines and estimate values for a_{CH_4} , σ_{CH_4} , ε_{CH_4} / k_B , a_{CO_2} , σ_{CO_2} , ε_{CO_2} / k_B , $\Delta \mu_0^{\text{EL-PW}}$ and $\Delta \overline{H}_0^{\text{EL-LW}}$. However, as we acknowledged the relation between $\Delta \overline{H}_w^{\text{EL-LW}}$ and the Langmuir constant parameters given by Equation (3.8), we included it in the estimation procedure and used calorimetric measurements besides the common three-phase equilibrium condition and occupancy experiments.

We, then, used four different sets of experiments. There are those that measure cage occupancy or hydrate guest composition at fixed conditions of pressure, temperature and gas and liquid phase composition – henceforth called occupancy experiments and guest mole fraction experiments, respectively. Those of calorimetric nature, which measure hydrate enthalpy of dissociation will be henceforth called enthalpy of dissociation experiments. Finally, we have those that give a set of pressure, temperature and gas and liquid phase composition of equilibrium – henceforth called equilibrium experiments. As it is illustrated in Figure 4, not all of them depend on the same set of parameters. Cage occupancy and guest mole fraction at fixed temperature, pressure and global composition is a function of the Langmuir constant parameters and $\Delta \overline{H}_0^{\text{EL-LW}}$ only. The equilibrium experiments are the only ones that yield quantities whose modeling depend on the complete set of parameters.



Figure 4 – Scheme of stepwise parameter estimation. In the first objective function concerning cage occupancy experiments and guest mole fraction, only Langmuir constant parameters are needed. In the second objective function including calorimetric experiments, the enthalpy change between the empty lattice and pure water is added to the set. Finally, in the third step, the whole set of parameters is estimate using equilibrium condition experiments.

One could possibly choose to minimize the whole set of parameters at the same time, by using an exhaustive minimization algorithm on the eight-dimensional parameter space. However, this is not an easy task since it would require a large quantity of evaluations – in order to increase reliability of a global optimization in an eight-dimensional space – of an effort-demanding objective function – because of the large amount of experimental data. Knowing from the homotopy continuation principle that the solution of simple problems is often a good guess for the solution of a more complex one, we chose to carry the estimation in a stepwise manner. Firstly, we used a stochastic algorithm (Particle Swarm Optimization – PSO)⁸³ to minimize the objective function regarding cage occupancy and guest molar fraction. Then, with this set of optimal parameters, we minimized the second objective function – regarding hydrate enthalpy of dissociation – with an analytical method, for the objective function of this step is linear with respect to the parameters. Finally, we obtained the optimal $\Delta \mu_0^{\text{EL-PW}}$ from the objective function regarding equilibrium conditions with all other parameters fixed also using an analytical solution. The set of parameters obtained after those three steps were the initial guess of the final problem that combined

all the experiments and the three objective functions by using an objective scalarization methodology proposed here. In the last step we used Nelder-Mead deterministic algorithm⁸⁴.

At the end of each step, we obtained the parameter confidence regions, using the methodology described by Schwaab *et al.*⁸³, which is represented in Equation (3.19).

$$F^{\text{obj}}\left(\underline{p}\right) \leq F^{\text{obj}}\left(\underline{p}^{*}\right) \left(1 + \frac{n_{\text{p}}}{n_{\text{exp}} - n_{\text{p}}} F_{n_{\text{p}}, n_{\text{exp}} - n_{\text{p}}}^{1-\alpha}\right)$$
(3.19)

In Equation (3.19), F stands for the Fisher distribution, α is the significance degree accepted in the analysis, n_p is the number of parameters being estimated, n_{exp} is the number of experiments, F^{obj} is the objective function, \underline{p} is the parameter vector and \underline{p}^* is the parameter vector at the minimum of the objective function. In this work, we used a default of 95% confidence or 0.05 significance degree.

Parametric correlation was then calculated from the confidence region points using the Pearson correlation coefficient definition. Other statistical metrics were also used to validate the proposed approach, namely the correlation coefficient between calculated and experimental values, the average absolute relative deviation and average absolute deviation. The remainder of this section introduces the three objective functions and the methodology used for combining them.

3.3.2. Cage Occupancy and Guest Mole Fraction Objective Function

In this step, we used a simple least squares objective function. It is represented in Equation (3.20).

$$F_{1}^{\text{obj}} = \sum_{i=1}^{n_{\text{exp},1}} \left(y_{i}^{\text{exp}} - y_{i}^{\text{calc}} \right)^{2}$$
(3.20)

3.3.3. Enthalpy of Dissociation Objective Function

The objective function used for obtaining the optimal value of $\Delta \overline{H}_{w}^{\text{EL-LW}}$ was the weighted least squares function. Differently from other experiments, all the calorimetric experiments included here had reported experimental uncertainties. The objective function is represented in Equation (3.21).

$$F_2^{\text{obj}} = \sum_{i=1}^{n_{\text{exp},2}} \left(\frac{\Delta \overline{H}_{\text{diss},i}^{\text{exp}} - \Delta \overline{H}_{\text{diss},i}^{\text{calc}}}{\sigma_i^{\Delta \overline{H}_{\text{diss}}}} \right)^2$$
(3.21)

If all Langmuir constant parameters are fixed, this becomes a linear problem with respect to $\Delta \overline{H}_0^{\text{EL-LW}}$ and its solution is such that respects the necessary optimality condition of null first derivative. Hence, from the differentiation of Equation (3.21), the optimal value of $\Delta \overline{H}_0^{\text{EL-LW}}$ for a fixed set of σ and $\varepsilon / k_{\text{B}}$ would respect the following relation.

$$\Delta \overline{H}_{0}^{\text{EL-LW}} = \frac{\sum_{i=1}^{n_{\exp,2}} \frac{\left(\Delta \overline{H}_{\text{diss},i}^{\exp} - \Delta \overline{U}_{i}^{\text{H-IG-EL}} \Gamma^{[0]} + RT_{i} + \overline{H}_{i}^{R,G} - \Gamma^{[1]}_{i}\right) \Gamma^{[0]}}{\left(\sigma_{i}^{\Delta \overline{H}_{\text{diss}}}\right)^{2}}$$

$$\frac{\Delta \overline{H}_{0}^{\text{EL-LW}} = \frac{\sum_{i=1}^{n_{\exp,2}} \left[\left(\sigma_{i}^{\Delta \overline{H}_{\text{diss}}}\right)^{2} \Gamma^{[0]}\right]}{\left(\sigma_{i}^{\Delta \overline{H}_{\text{diss}}}\right)^{2}} \Gamma^{[0]}$$

$$(3.22)$$

In which:

$$\Delta \overline{U}^{\text{H-IG-EL}} = RT^2 \sum_{n=1}^{n_{\text{guest}}} \sum_{m=1}^{n_{\text{cage}}} \nu_m \theta_{m,n} \left[\frac{\partial}{\partial T} \ln \left(C_{m,n} k_{\text{B}} T \right) \right]$$
(3.23)

$$\Gamma^{[0]}_{i} = \left(\frac{1 - \sum_{j=1}^{n_{\text{guest}}} x_{j,i}^{\text{H}}}{\sum_{j=1}^{n_{\text{guest}}} x_{j,i}^{\text{H}}}\right)$$
(3.24)

$$\Gamma_{i}^{[1]} = \Delta C p_{0}^{\text{EL-PW}} \left(T_{i} - T_{0} \right) + \Delta B_{0}^{\text{EL-PW}} \left(\frac{T_{i}^{2}}{2} - \frac{T_{0}^{2}}{2} \right) + \left[\int_{P_{0}}^{P_{i}} \Delta \overline{V}^{\text{EL-PW}} - T_{i} \left(\frac{\partial \Delta \overline{V}^{\text{EL-PW}}}{\partial T} \right) dP \right]$$
(3.25)

3.3.4. Equilibrium Experiments Objective Function

The usual hydrate-liquid-vapor phase equilibrium is calculated from the chemical potential equalities that depend on all eight parameters, as seen in the Section 2.2. The following indirect least squares objective function was used – Equation (3.26) –, following the approach developed by Oliveira *et al.*⁸⁵. With all other parameters fixed, this also becomes a linear problem.

$$F_{3}^{\text{obj}} = \sum_{i=1}^{n_{\text{exp},3}} \left(\frac{\Delta \mu_{\text{w}}^{\text{EL-PW}}}{-\Delta \mu_{\text{w}}^{\text{H-EL}}} - 1 \right)^{2}$$
(3.26)

Using the same approach as in Section 2.3.3, we obtain its analytical solution:

$$\frac{\Delta \mu_{0}^{\text{EL-PW}}}{RT_{0}} = \frac{\sum_{i=1}^{n_{\text{exp,3}}} \left[\frac{1}{\frac{\Delta \mu_{w,i}^{\text{H-EL}}}{RT_{i}}} + \frac{-\int_{T_{0}}^{T_{i}} \frac{\Delta \overline{H}^{\text{EL-PW}}}{RT^{2}} dT + \int_{P_{0}}^{P_{i}} \frac{\Delta \overline{V}^{\text{EL-PW}}}{RT} dP}{\left(\frac{\Delta \mu_{w,i}^{\text{H-EL}}}{RT_{i}}\right)^{2}} \right]}{\sum_{i=1}^{n_{\text{exp,3}}} \frac{1}{\left(\frac{\Delta \mu_{w,i}^{\text{H-EL}}}{RT_{i}}\right)^{2}}}{\left(\frac{\Delta \mu_{w,i}^{\text{H-EL}}}{RT_{i}}\right)^{2}}$$
(3.27)

This objective function deserves some comments. Usually on estimation problems, directly measured values of a given variable are compared to the ones obtained by the model from which the parameters are being estimated. However, here we opted to compare calculated chemical potential ratios to the ones obtained experimentally at a given temperature, pressure and composition, which equals 1. This procedure gives some advantages. Firstly, there is no hierarchy on which measured variable is regarded as input and output of the model. This is important for the hydrate phase equilibrium has some particularities. In general, reported errors in temperature measurements are lower than those in pressure and, for that reason, temperature would be a natural input variable. However, at temperatures above hydrate retrograde dissociation point, there is not a pressure solution for a given set of temperature and composition. In addition, comparing chemical potential equalities makes it possible to avoid expensive computational effort, as there is no need to solve the chemical potential equality for pressure, temperature or composition using root-finding algorithms. These algorithms would require several iterations that in turn depend on other iterative numerical methods, such as integrators, and ultimately might not lead to a solution.

3.3.5. Global Objective Function

There are infinite ways to combine the three aforementioned objective functions. In this work, we did not want to create any bias towards a certain type of experiment. This could have been done by using a weighted least squares function. However, some of our variables are indirect and others do not present coherent uncertainties. Thus, we proposed the following heuristic methodology as a way to avoid producing a set of parameters that describes well some phenomena

at the expense of others. This methodology, however, can be objectively applied to different problems involving several objective functions to take into account.

If one would approximate an objective function by its corresponding Taylor series, one would obtain the following expression in matrix notation:

$$F_{g}^{obj} = F_{g}^{obj}\Big|_{p^{*}} + \nabla F_{g}^{obj}\Big|_{p^{*}} \underline{\Delta p} + \frac{1}{2} \underline{\Delta p}^{\mathrm{T}} \nabla^{2} F_{g}^{obj}\Big|_{p^{*}} \underline{\Delta p}$$
(3.28)

However, knowing that the necessary condition to find an optimal point of a function is that its first derivative is zero with respect to all parameters, Equation (3.28) could be replaced by:

$$F_{g}^{obj} = F_{g}^{obj}\Big|_{\underline{p}^{*}} + \frac{1}{2}\underline{\Delta p}^{T}\nabla^{2}F_{g}^{obj}\Big|_{\underline{p}^{*}}\underline{\Delta p}$$
(3.29)

Optimization algorithms in a general manner will search for the steepest descent of the objective function hyper surface. To combine all three objective functions in an unbiased manner, we proposed weights based on the second order derivative. Those weights act to even the magnitude of deviations from the optimal solution and they smooth the search for a steepest descent so that none of the objective functions is prioritized due to its naturally higher value. We defined the global objective function as follows.

$$F_{\rm g}^{\rm obj} = w_1 F_1^{\rm obj} + w_2 F_2^{\rm obj} + w_3 F_3^{\rm obj}$$
(3.30)

Then, the following relation must be true around the optimal solution:

$$\Delta F_{g}^{obj} = \frac{w_{1}}{2} \underline{dr}^{\mathrm{T}} \nabla^{2} F_{1}^{obj} \underline{dr} + \frac{w_{2}}{2} \underline{dr}^{\mathrm{T}} \nabla^{2} F_{2}^{obj} \underline{dr} + \frac{w_{3}}{2} \underline{dr}^{\mathrm{T}} \nabla^{2} F_{3}^{obj} \underline{dr}$$
(3.31)

If F_1^{obj} , F_2^{obj} and F_3^{obj} contribute equally to the global objective function, then an infinitesimal variation in the parameter space should give rise to contributions of F_1^{obj} , F_2^{obj} and F_3^{obj} of the same order of magnitude. Therefore, the terms w_1 , w_2 and w_3 must satisfy the following conditions:

$$\begin{cases} w_1 \underline{dr}^{\mathrm{T}} \nabla^2 F_1^{\mathrm{obj}} \underline{dr} = w_3 \underline{dr}^{\mathrm{T}} \nabla^2 F_3^{\mathrm{obj}} \underline{dr} \\ w_2 \underline{dr}^{\mathrm{T}} \nabla^2 F_2^{\mathrm{obj}} \underline{dr} = w_3 \underline{dr}^{\mathrm{T}} \nabla^2 F_3^{\mathrm{obj}} \underline{dr} \end{cases}$$
(3.32)

In which <u>dr</u> is a vector containing plausible deviations in the parameter space. By plausible deviations, we mean the difference between the upper and lower bounds of a given parameter that would lead to F_1^{obj} , F_2^{obj} and F_3^{obj} within the limit stipulated by Equation (3.19) when all other parameters are held constant.

This work was developed in IPython⁸⁶ and the scientific library SciPy⁸⁷ contains the algorithms used. Figures were created using Matplotlib⁸⁸.

3.3.6. Experimental Data

Experimental data used in this work is listed in Table 3.

	Number of	Objective Function	References
	Experiments		
Cage Occupancy	30	$F_1^{\rm obj}$ and $F_g^{\rm obj}$	89–91
Guest mole fraction	24	$F_1^{\rm obj}$ and $F_g^{\rm obj}$	31,32,42,92–95
Enthalpy of	4	$F_2^{\rm obj}$ and $F_g^{\rm obj}$	31,32
Dissociation from			
Calorimetry			
Equilibrium	321	$F_3^{\rm obj}$ and $F_g^{\rm obj}$	96
Conditions – Methane			
Equilibrium	212	$F_3^{\rm obj}$ and $F_g^{\rm obj}$	96
Conditions – Carbon			
Dioxide			
Equilibrium	164	$F_3^{\rm obj}$ and $F_g^{\rm obj}$	96
conditions – Methane			
+ Carbon Dioxide			

Table 3 – Experimental data used for parameter estimation.

4. Results and Discussion

4.1. First Step

In the first step of the parameter optimization, we fitted the Langmuir constant parameters using occupancy and guest mole fraction experiments. This is an important step to diminish hydrate parameter correlation since it depends only on the Langmuir constant parameters.

In a first attempt, we used the Kihara Potential with parameters a, σ and $\varepsilon / k_{\rm B}$. However, results were not satisfactory. Firstly, we observed the occurrence of several different local minima that should be within the confidence region according to Equation (3.19). Some of them are displayed in Table 4. Furthermore, we noted a high degree of correlation among the Kihara parameters. Figure 5 shows the confidence regions of all three parameter when two of them are varying and the others are held constant at the optimal values. It shows the relation between a, σ and $\varepsilon / k_{\rm B}$ for the two guests studied in our work. It can be seen that all three parameters are strongly correlated and that the confidence region for a includes zero, meaning that the absence of this parameters is as statistically significant as its presence. Quantitative measures of correlation are also displayed in Table 5. After that, we decided to use the Lennard-Jones potential, i.e. a equals zero.

Minim	Minima found with Kihara Potential				Minin	num fo	ound w	vith Le	nnard-		
				Jones	Potenti	al					
F_1^{obj}	$a_{_{CH_4}}/\text{\AA}$	$\sigma_{_{CH_4}}/{ m \AA}$	$\frac{\varepsilon_{_{CH_4}}}{k_{_{\rm B}}}/{ m K}$	$a_{co_2}/\text{\AA}$	$\sigma_{_{CO_2}}/ m \AA$	$\frac{\varepsilon_{co_1}}{k_{\rm B}}/{\rm K}$	$F_1^{ m obj}$	$\sigma_{_{CH_4}}/{ m \AA}$	$\frac{\mathcal{E}_{_{CH_4}}}{k_{_{\rm B}}}$ / K	$\sigma_{_{CO_2}}/\text{\AA}$	$\frac{\varepsilon_{_{CO_2}}}{k_{_{\rm B}}}/{ m K}$
0.098	0.665	2.916	150.6	0.00	3.541	146.8	0.100	3.523	141.7	3.540	146.7
0.104	0.0813	3.534	165.7	0.022	3.559	156.3	0.100	3.523	141.7	3.540	146.7
0.091	2.770	1.034	173.9	2.201	1.546	198.9	18.97	0.0405	24071	0.6002	9598.3
0.094	1.731	1.958	147.0	0.00	3.541	147.0	0.100	3.523	141.7	3.540	146.7
0.099	0.435	3.125	146.7	0.00	3.540	146.7	0.100	3.523	141.7	3.540	146.7

Table 4 – Minima found in the first step of parameter estimation.



Figure 5 – Confidence regions of Kihara potential parameters. Orange regions represent confidence regions for CO₂ parameters and blue regions represent confidence regions for methane parameters. Parameter units were omitted for simplicity but they are the same as in Table 2.

	a_{CH_4}	$\sigma_{_{CH_4}}$	$arepsilon_{CH_4}$ / $k_{ m B}$	a_{CO_2}	$\sigma_{_{CO_2}}$	$arepsilon_{CO_2}$ / $k_{ m B}$
a_{CH_4}	1.000000	-0.976251	0.973592	-0.007340	-0.007340	-0.010577
$\sigma_{_{CH_4}}$	-0.976251	1.000000	0.973641	-0.007981	-0.007981	-0.010577
$arepsilon_{CH_4}$ / $k_{ m B}$	0.973592	0.973641	1.000000	0.033592	0.033592	-0.009745
a_{CO_2}	-0.007340	-0.007981	0.033592	1.000000	-0.930227	0.949807
$\sigma_{_{CO_2}}$	-0.007340	-0.007981	0.033592	-0.930227	1.000000	0.959835
$\varepsilon_{CO_2}/k_{ m B}$	-0.010577	-0.010577	-0.009745	0.949807	0.959835	1.000000

Table 5 - Correlation matrix of Kihara parameters.

Estimation using the Lennard-Jones potential was more successful that using the Kihara potential. We found only one minimum using PSO algorithm and the confidence regions did not

include zero, as it happened with the Kihara potential. We also used the Nelder-Mead deterministic algorithm to find Lennard-Jones parameters using the Kihara σ and $\varepsilon / k_{\rm B}$ optimal values as initial estimates. All attempts converged to the same minimum (Table 4), indicating that the Lennard-Jones potential was a better choice than the Kihara potential.

Nonetheless, the Lennard-Jones potential also presents a high degree of correlation between σ and $\varepsilon/k_{\rm B}$ in the scenario we studied. In Figure 6, we displayed the confidence regions of all possible pairs of Lennard-Jones parameters. Orange regions are the confidence regions when two parameters are varying and the others are held constant at the optimal values. Blue regions are the projection of confidence regions when all parameters are varying. Parameters of the same guest are very correlated and their functionality seems to be an exponential. Parameters of different guests seem to be independent, as they originate circular confidence regions. One of the reasons for these two phenomena might be the greater quantity of occupation and guest mole fraction experiments involving simple hydrates used in the estimation. Table 6 shows the Pearson correlation coefficient for all pairs of Lennard-Jones parameters calculated from the orange regions in Figure 6. It quantitatively confirms what have been stated by analyzing Figure 6.

	$\sigma_{_{CH_4}}$	$arepsilon_{CH_4}$ / $k_{ m B}$	$\sigma_{_{CO_2}}$	$arepsilon_{CO_2}$ / $k_{ m B}$
$\sigma_{_{CH_4}}$	1.000000	0.899352	-0.016232	0.034393
$arepsilon_{CH_4}$ / $k_{ m B}$	0.899352	1.000000	-0.038440	0.002905
$\sigma_{_{CO_2}}$	-0.016232	-0.038440	1.000000	0.955657
$\varepsilon_{_{CO_2}}$ / $k_{_{ m B}}$	0.034393	0.002905	0.955657	1.000000

Table 6 – Correlation matrix after for Lennard-Jones parameters.



Figure 6 – Confidence regions of Lennard-Jones potential parameters. Orange markers represent confidence regions with two parameters varying and the others fixed at the optimal values. Blue markers represent confidence regions with all parameters varying. Insets show both confidence regions close to the optimal point in detail. Parameter units were omitted for simplicity but they are the same as in Table 2.

From this minimization step, we obtained the following values for σ and $\varepsilon / k_{\rm B}$ and their limits according to Equation (3.19) (Table 7).

Parameter	Optimal Value	Lower Bound	Upper Bound
$\sigma_{_{CH_4}}/{ m \AA}$	3.523	3.484	3.553
$\frac{\mathcal{E}_{CH_4}}{k_{ m B}}/ m K$	141.675	136.048	147.934
$\sigma_{\scriptscriptstyle CO_2}/{ m \AA}$	3.540	3.493	3.578
$\frac{\varepsilon_{CO_2}}{k_{\rm B}}/{\rm K}$	146.743	138.523	155.643

Fable	7	– Final	results	of	step	1.

4.2. Second Step

In this step, we minimized objective function F_2^{obj} with fixed Langmuir constant parameters. From this step, we obtained the optimal value of $\Delta \overline{H}_0^{\text{EL-LW}}$ and its limit values represented in Table 8.

Parameter	Optimal Value	Lower Bound	Upper Bound
$\Delta \overline{H}_{0}^{\text{EL-LW}} / (\mathrm{J} \times \mathrm{mol}^{-1})$	-5173.6	-5776	-4441

Table 8 – Final results of step 2

Before moving to step 3, we carried another study in order to verify the effect of including calorimetric experiments in parametric correlation. Parametric correlation can only be correctly assessed close to a minimum. In order to do it, we combined F_1^{obj} and F_2^{obj} in an manner analogous to that described in Section 2.3.5 and minimized the combined function. The minimum and the confidence region are depicted in Figure 7. The parametric correlation for each pair of parameters is displayed in Table 9. As it can be seen, the inclusion of this new set of experiments led to a great diminution of parametric correlation among the Lennard-Jones parameters.

	$\sigma_{_{CH_4}}$	$arepsilon_{CH_4}$ / $k_{ m B}$	$\sigma_{{}_{CO_2}}$	$\varepsilon_{_{CO_2}}$ / $k_{_{ m B}}$	$\Delta \overline{H}_0^{ ext{EL-LW}}$
$\sigma_{_{CH_4}}$	1.000000	0.362214	-0.019804	-0.032089	0.613498
$arepsilon_{CH_4}$ / $k_{ m B}$	0.362214	1.000000	-0.005672	0.003461	0.261060
$\sigma_{_{CO_2}}$	-0.019804	-0.005672	1.000000	0.394594	0.439042
$arepsilon_{CO_2}$ / $k_{ m B}$	-0.032089	0.003461	0.394594	1.000000	0.159262
$\Delta \overline{H}_0^{ ext{EL-LW}}$	0.613498	0.261060	0.439042	0.159262	1.000000

Table 9 – Correlation matrix after the second step.



Figure 7 – Confidence regions after step 2 (Occupancy and guest mole fraction experiments + calorimetric experiments). Orange markers represent confidence regions with two parameters varying and the others fixed at the optimal values. Blue markers represent confidence regions with all parameters varying. Parameter units were omitted for simplicity but they are the same as in Table 5 and Table 6.

4.3. Third Step

From the set of Langmuir constant parameters and $\Delta \overline{H}_0^{\text{EL-LW}}$, the chemical potential difference between water and the empty lattice was estimated. The parameter obtained and its limit values are listed in Table 10.

Parameter	Optimal Value	Lower Bound	Upper Bound
$\Delta \mu_{\scriptscriptstyle W}^{\scriptscriptstyle \mathrm{EL-PW}} / (\mathrm{J} imes \mathrm{mol}^{-1})$	1075.79	1070.78	1080.8

Table 10 – Final results of step 3.

4.4. Global Estimation Results

The parameters obtained from the global estimation procedure are listed in Table 11, along with the initial estimates. Table 11 also compares them to values obtained by other authors. σ and $\varepsilon/k_{\rm B}$ are close to the values reported in literature. However, $\Delta \overline{H}_0^{\rm EL-LW}$ and $\Delta \mu_0^{\rm EL-PW}$ are considerably different from literature that were estimated from hydrate equilibrium data. Their values, nonetheless, approach the ones obtained by molecular simulation from Jacobson, Hujo and Molinero⁹⁷.

Table 12 shows the weighted objective functions prior to and after the last estimation step. From this table, one can see that the description of hydrate enthalpy of vaporization and hydrate equilibrium conditions were enhanced in expense of the description of cage occupancies and guest molar fractions. This was already expected because the initial guess came from a an optimal F_1^{obj} value that did not depend on $\Delta \overline{H}_0^{\text{EL-LW}}$ and $\Delta \mu_0^{\text{EL-PW}}$, while F_2^{obj} and F_3^{obj} were minimized with σ and ε / k_B held constant. Another interesting result is that the stepwise objective functions approach 0.6, contributing in the same order of magnitude to the global result.

Reference	a_{CH_4} /Å	$\sigma_{_{CH_4}}/ m \AA$	$\frac{\mathcal{E}_{CH_4}}{K}$	$a_{CO_2}/\text{\AA}$	$\sigma_{\scriptscriptstyle CO_2}/{ m \AA}$	$\frac{\mathcal{E}_{CO_2}}{K}$	$\Delta \overline{H}_{_0}^{_{ m EL-LW}}$ /	$\Delta \mu_{_{\scriptscriptstyle W}}^{_{\scriptscriptstyle m EL-PW}}$ /
			k _B			k _B	$(J \times mol^{-1})$	$\left(J \times mol^{-1} \right)$
Optimal	0	3.373	130.491	0	3.537	137.318	-5363.9	797.33
Parameters								
Initial Guess	0	3.523	141.675	0	3.540	146.743	-5173.6	1075.79
14	0.230	3.533	142.119	0.677	3.486	227.388	-4297	1120
45	0.3834	3.17784	154.923	0.6805	2.97175	176.242	-	-
98	0.260	3.601	141.298	0.677	3.450	184.558	-	-
97	-	-	-	-	-	-	-5473	714

Table 11 - Comparison between parameters obtained in this work and in literature.

Table 12 - Weighted global objective function prior to and after global estimation.

	Initial Guess	Minimum Found
$F_1^{ m obj}$	0.245491	0.6002808
$F_2^{ m obj}$	2.748847	0.6347308
$F_3^{ m obj}$	1.968253	0.6015880
$F_g^{ m obj}$	4.962592	1.8365997

Parametric correlation can be observed quantitatively in Table 13 and qualitatively in Figure 8. From Figure 8, we see that most of the confidence regions approach circles or uncorrelated ellipses. Parameters σ and $\varepsilon/k_{\rm B}$ for methane still present a high degree of correlation (Pearson correlation coefficient of -0.838428) and their correlation is higher than observed in step 2. The two parameters also became negatively correlated after the global estimation. Highly correlated pairs of parameters include $\Delta \mu_0^{\rm EL-PW}$: $\varepsilon_{CO_2}/k_{\rm B}$ and $\Delta \mu_0^{\rm EL-PW}$; $\varepsilon_{CH_4}/k_{\rm B}$ and $\Delta \mu_0^{\rm EL-PW}$; and σ_{CH_4} and $\Delta \mu_0^{\rm EL-PW}$. This should be expected, as there is only one type of experiment that involves this parameter. One can see that those parameters that can be obtained

from different experiments present lower degrees of correlation. Figure 8 also displays the approximate confidence intervals of parameters with 95% confidence in the legends of each graph.

	$\sigma_{_{CH_4}}$	$arepsilon_{CH_4}$ / $k_{ m B}$	$\sigma_{\scriptscriptstyle CO_2}$	$\varepsilon_{_{CO_2}}$ / $k_{_{ m B}}$	$\Delta \overline{H}_w^{ ext{EL-LW}}$	$\Delta\mu_{\scriptscriptstyle W}^{\scriptscriptstyle m EL-PW}$
$\sigma_{_{CH_4}}$	1.000000	-0.838428	0.021386	-0.058750	0.292511	0.602950
$arepsilon_{CH_4}$ / $k_{ m B}$	-0.838428	1.000000	0.029726	-0.095267	-0.144836	0.683058
$\sigma_{_{CO_2}}$	0.021386	-0.005672	1.000000	0.253835	0.477904	-
						0.025630
$arepsilon_{CO_2}$ / $k_{ m B}$	-0.058750	-0.095267	0.253835	1.000000	-0.072771	0.715731
$\Delta \overline{H}_w^{ ext{EL-LW}}$	0.292511	-0.144836	0.477904	0.159262	1.000000	0.075560
$\Delta\mu_{\scriptscriptstyle W}^{\scriptscriptstyle m EL-PW}$	0.602950	0.683058	-0.025630	0.715731	0.075560	1.000000

 Table 13 – Parametric correlation after global estimation.



Figure 8 – Confidence regions after global estimation (all experiments included in the weighted objective function). Orange markers represent confidence regions with two parameters varying and the others fixed at the optimal values. Blue markers represent confidence regions with all parameters varying. Approximate confidence intervals of parameters are displayed in the legends of each graph. Parameter units were omitted for simplicity but they are the same as in Table 9.

Figure 9 compares the experimental values of cage occupancy to the ones calculated using the new parameters. The model does not provide a very good agreement to experimental data, as the points are scattered around the quadrant bisector and the correlation coefficient between experimental and calculated values is not close to unity. The same happened to the guest mole fraction. Although the correlation coefficient was slightly higher, it is still considerably far from unity. In most cases, the model underestimates guest mole fraction (Figure 10). As it was mentioned earlier here, these experiments are somewhat discrepant and this might account to the poor prediction performance. Quantitative measures of disagreement are reported in Table 14 as a supplement to the figures.

Calculated hydrate enthalpy of dissociation is in good agreement to experimental data. As it can be seen in Figure 11, the model yielded results within the error bars of three of the four experiments used in parameter estimation. The mean absolute deviation was around 1.14 kJ/mol of gas, the same magnitude of the mean experimental error (1.17 kJ/mol of gas)

The analysis of equilibrium experiments was split into three different parts to avoid misinterpretation of the results. For methane, Figure 12 shows that the model presents a good agreement in low temperatures, while it underestimates equilibrium temperature at higher temperatures. This is due to the poor accuracy of the model at high pressures. This phenomenon can be better understood by analyzing Figure 13, which shows the pressure-temperature diagram for methane hydrates in excess of water. At low pressures, the full line that represents predicted equilibrium temperatures for a given pressure is very close to the markers representing experimental data. It is only above 1×10^8 Pa that the model seriously deviates from experimental data. One of the reasons for the poor performance is hydrate retrograde dissociation and the modelling of volume changes. The Clapeyron equation states that the increment of the saturation pressure curve with temperature depends on the enthalpy change of phase transition and the volume change of phase transition.

$$\frac{dP}{dT} = \frac{\Delta \overline{H}_{\text{diss}}}{T \Delta \overline{V}_{\text{diss}}}$$
(4.1)

Hence, hydrate retrograde dissociation can only start at the point in which $\Delta \overline{V}_{diss}$ equals zero. The dashed line in Figure 13 is a set of points in which $\Delta \overline{V}_{diss}$ is zero according to the phase modeling used in our work and the following equation:

$$\Delta \overline{V}_{\text{diss}} = x_{\text{max}}^{\text{H}} \overline{V}^{G} + \overline{V}^{LW} - \overline{V}^{EL}$$
(4.2)

In this equation, x_{max}^{H} is the maximum guest molar fraction, that is, when the total cage occupancies for both small and large cages approach unity. It shows that the combination of the equation of state for the gas phase and the volume correlations for the liquid and the hydrate phase cannot accurately describe this phenomenon, as the dashed line does not cross the experimental dispersion at the retrograde dissociation point. Figure 13 also shows that correct phase volume description would not suffice to model equilibrium at such high pressures, meaning that there is still room for improvement in the calculation of enthalpies for each phase. Despite this, the correlation coefficient between experimental and calculated values approaches unity and the mean absolute deviation including points at high pressure is less than 2 K.

For carbon dioxide simple hydrates (Figure 14 and Figure 15), the correlation coefficient was even closer to unity and the mean absolute deviation was lower than 1K. The best results in terms mean absolute deviation, however, were those for mixed hydrates. In this scenario, mean absolute deviation was lower than 0.5K and the correlation coefficient between experimental and calculated values was 0.9834. Those two metrics are apparently incoherent, but they can be understood by analyzing Figure 16. This figure shows that the majority of points are near the quadrant bisector, lowering the average deviation, while only a few points are considerably far from it, diminishing the value of the correlation coefficient.

Property	Average Absolute	Average Absolute	Correlation
	Relative Deviation	Deviation	Coefficient
	(%)		
Cage	6.426	0.051	0.882
Occupancy			
Guest mole	10.18	0.011	0.975
fraction			
Enthalpy of	1.809	1.060 (kJ/mol of gas)	0.961
Dissociation			
from			
calorimetry			
Equilibrium	0.552	1.603 K	0.995
Temperature -			
Methane			
Equilibrium	0.311	0.802 K	0.998
Temperature –			
Carbon Dioxide			
Equilibrium	0.129	0.358 K	0.983
Temperature –			
Methane +			
Carbon Dioxide			

Table 14 – Statistical metrics for the quality of the estimation procedure.



Figure 9 – Comparison between measured and calculated values of occupation fraction. Experimental data from Kuhs *et al.*⁸⁹; Qin and Kuhs⁹⁰; and Uchida *et al.*⁹¹.



Figure 10 – Comparison between measured and calculated values of guest mole fraction. Experimental data from Kang, Lee and Ryu³¹; Lievois *et al.*³²; Yoon *et al.*⁴²; Handa⁹²; Rueff, Sloan and Yesavage⁹³; Circone *et al.*⁹⁴; and Henning *et al.*⁹⁵



Figure 11 – Comparison between measured and calculated values of enthalpy of dissociation. Experimental data from Kang, Lee and Ryu³¹ and Lievois *et al.*³²



Figure 12 – Comparison between measured and calculated values of equilibrium temperature for methane hydrates. Experimental data from NIST⁹⁶.



Figure 13 – Hydrate-liquid-gas three-phase equilibrium line for methane hydrates. Experimental data from NIST⁹⁶.



Figure 14 – Comparison between measured and calculated values of equilibrium temperature for carbon dioxide hydrates. Experimental data from NIST⁹⁶.



Figure 15 – Hydrate-liquid-gas three-phase equilibrium line for carbon dioxide hydrates. Experimental data from NIST⁹⁶.



Figure 16 – Comparison between measured and calculated values of equilibrium temperature for methane + carbon dioxide hydrates. Experimental data from NIST⁹⁶.

4.5. Comments on Hydrate Enthalpy of Dissociation

After addressing the results from parameter estimation, we can make some comments on hydrate enthalpy of dissociation. Some experimental works report hydrate enthalpy of dissociation without its corresponding values of equilibrium temperature and pressure³⁶. This is mostly due to experimental difficulties regarding calorimetric experiments. In Figure 17, we display several enthalpy of dissociation experimental data together with predicted isotherms. The pressure used for calculating enthalpy of dissociation was that of the hydrate three-phase equilibrium at a given *T* and a given carbon dioxide gas mole fraction. However, in order to compare calculations to experimental data, the x-axis in Figure 17 shows CO₂ hydrate mole fraction in a guest basis, i.e. discounting water present in the structure. From Figure 17, we see that the experimental data discrepancies are not inconsistent, as it might appear. The model predicts a considerably large range of values for enthalpy of dissociation and if temperature and pressure are not controlled, measurements can be scattered throughout the whole range.



Figure 17 – Enthalpy of dissociation of methane + carbon dioxide hydrates. Pressure used for calculation was the equilibrium pressure at fixed temperature and CO₂ gas mole fraction. X-Axis shows CO₂ hydrate fraction in guest basis (discounting water in the hydrate phase). Experimental data from Lee *et al.*³⁶, Rydzy *et al.*³³ and Kwon *et al.*⁹⁹.

Figure 17 also shows that for most of the isotherms, the rise in CO₂ mole fraction causes the rise in enthalpy of dissociation. However, an interesting phenomenon occurs at the 285.0 K isotherm. There is an abrupt interruption around 90% CO₂ hydrate mole fraction and after the discontinuity, the increase in mole fraction engenders a diminution of enthalpy of dissociation. This is probably related to the phase transition of the CO₂-rich gas to a CO₂-rich liquid. It is reasonable to suppose so because the second quadruple point of CO₂ is around 285.0 K. Isotherms at higher temperatures change their behavior smoothly in a supercritical-like manner. It should be noted, however, that the only liquid modelled during parameter estimation was liquid water and that the solubility of carbon dioxide in water and water in carbon dioxide was neglected. This means that quantitative information when other liquids are present might not be reliable.

Figure 18 brings about a new point of view to this discussion. From Equation (3.8), we identify two major contributions to the enthalpy of dissociation. The enthalpy of disenchlatrating

a given gas – representing the terms
$$\sum_{j=1}^{n_{guest}} x_j^{H} \overline{H}_j^{R} + RT \sum_{j=1}^{n_{guest}} x_j^{H} - x_w^{H} RT^2 \sum_{j=1}^{n_{guest}} \sum_{i=1}^{n_{guest}} v_i \theta_{i,j} \left[\frac{\partial}{\partial T} \ln \left(C_{i,j} k_{B} T \right) \right]$$

of Equation (3.8), but by gas mole fraction – and the enthalpy of melting the empty hydrate structure – representing the term $\left(-x_{w}^{H}\Delta \overline{H}_{w}^{\text{EL-PW}}\right)$ of Equation (3.8), but by gas mole fraction. It is clear from Figure 18 that water contributes the most to the enthalpy change, but the abrupt transition at 90% CO₂ gas mole fraction comes from the guest contribution, indicating a phase change.



Figure 18 – Total enthalpy of dissociation of mixed methane + carbon dioxide hydrates and the energetic contribution of water and guests.

It has been argued that hydrate enthalpy in binary mixtures depends mostly on the occupation of large cavities^{33,36,43}. Figure 19 is an attempt to verify this affirmation. In each pair of diagram it presents, all properties were calculated at constant temperatures. The full blue lines on the left hand diagrams represent hydrate enthalpy of dissociation and it reports to the left hand side y-axis. The green dashed line represents the equilibrium pressure at fixed temperature and CO₂ gas mole fraction. The right hand diagrams represent cage occupancy of methane and carbon dioxide as a function of CO₂ gas mole fraction. Temperature and pressure in which they were calculated are represented in the corresponding left hand side diagram. The red dotted line and the yellow dash-dotted line represent the occupation fraction of carbon dioxide in the large and small

cavities, respectively. The full light blue line and the dashed dark blue line represent the occupation fraction of methane in the large and small cavities, respectively.

In the first diagram at 280.00 K, the carbon dioxide occupation fraction of large cavities is positively correlated to the enthalpy of dissociation. It can also be seen that the enthalpy of dissociation is negatively correlated to the equilibrium pressure throughout the whole range of CO_2 gas mole fraction.

At 285.00 K, those relations become less clear as illustrated in the second diagrams of Figure 19. Occupation of large cavities by CO_2 increases with higher percentages of CO_2 in the gas phase throughout the whole diagram. This positive correlation is also true for enthalpy of dissociation, until the aforementioned discontinuity. After that point, the correlation between enthalpy of dissociation and CO_2 gas mole fraction is negative. The same kind of inversion happens to the equilibrium pressure. Before the discontinuity, equilibrium pressure lowers with an increase in CO_2 in the gas phase. Apparently, the only relation that holds before and after the phase change is the negative correlation between equilibrium pressure and enthalpy of dissociation.

In the third diagram of Figure 19, the non-trivial relation between amongst these properties becomes even more evident as the gas transit smoothly from a gas-like phase to a liquid-like phase. However, this non-clear dependency should be expected. After all, the dissociation enthalpy is a function of the molar enthalpy of the three phases involved in equilibrium. Therefore, if the enthalpy of gases and liquids is sensitive to rises in pressure and temperature, these properties will contribute in their own manner to the behavior of the enthalpy of dissociation.

The evolution of methane occupation fraction is also interesting. Closer to pure methane (low CO_2 gas mole fraction) methane occupation fraction in large cavities is greater than in small cavities. However, with increasing amount of CO_2 in the gas phase, methane tends to occupy small cavities rather than large ones. At higher temperatures, this inversion happens with lower amounts of CO_2 .



Figure 19 – Evaluation of pressure, temperature and cage occupancy effects on mixed hydrates enthalpy of dissociation.

5. Conclusions

In this work, we derived an expression for hydrate enthalpy of dissociation directly from the van der Waals and Platteeuw Statistical Thermodynamics model. This expression allows the calculation of hydrate enthalpy of dissociation at any equilibrium conditions for any gas mixture without introducing any other parameters.

We also used this expression to include calorimetric experiments into hydrate parameter estimation. We then proposed a stepwise parameter estimation and the calorimetric experiments proved useful for accelerating the estimation convergence, as we did not have to use exhaustive optimization methods.

The first step of the parameter estimation showed that, for the binary clathrates studied here, the hard-core parameter of the Kihara potential was not statistically significant and we opted to use the Lennard-Jones potential. As it was shown in the results section, the use of the Lennard-Jones potential did not compromise the model performance, as it was able to predict hydrate properties in a wide range of conditions.

Even without the hard-core parameter, the Langmuir constant parameters presented a high degree of correlation. However, the second step sufficed to diminish parametric correlation to a satisfactory level.

Finally, we showed that the van der Waals and Platteeuw model predicts the empirical observation that the cage occupation by a larger guest yields a higher enthalpy of dissociation. However, this was not valid throughout the whole range of temperature studied. We saw that the fluid phases also have an impact on this property.

Future work on the model could focus on the inclusion of different kinds of experiments in parameter estimation. Gas hydrate crystallographic measurements could be included in an attempt to reduce parameter correlation. However, this would need further investigation on the van der Waals and Platteeuw model.

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