EHSAN HEIDARYAN

Kinetic study on gas hydrate formation and dissociation

São Paulo

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Revised Version

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To my family for everything!

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ABSTRACT

HEIDARYAN, E. **Kinetic study on gas hydrate formation and dissociation**. 2020. 170 p. D.Sc. Thesis- Chemical Engineering, Polytechnic School, University of São Paulo, São Paulo, 2020.

In 1884, Jacobus Henricus van't Hoff and Henry Louis Le Chatelier started the race for understanding chemical kinetics and equilibrium. Consequently, the scientific prowling for coming up direction, stability, and ending point of chemical reactions has not stopped. Equilibrium and kinetic of gas hydrates (also called clathrates), which are crystalline structures formed by light gas molecules (guest) enclosed by water molecules linked by hydrogen bonds, are part of this great race. Accurate knowledge of equilibrium and kinetic of gas hydrates is vital in both flow assurance of transport lines and energy production from the seabed. Traditionally, most of gas hydrates kinetic studies determine the moles of gas consumed from pressure changes measurements when the gas is getting dissolved into water to form the hydrate in an isolated system. So, in this research, a study in a standard reactor has been carried out to evaluate methane hydrate formation and dissociation at 276.2 K and various pressures of 2700, 2900 and 3200 kPa. Among many studied parameters, the second moment of the particle size distribution ($\mu_2(t)$) is the key factor to understand the properties of the produced gas hydrate even there is a wide crystal size distribution in practice, since it is related to the kinetic constant. The main objective of this dissertation is to determine methane hydrate $\mu_2(t)$ based on an analytical model deduced from mass balance. In the construction of the current model, parameters of hydration number, the molar volume of gas hydrates, the initial amount of water contained in the system, and the total number of moles of reacted water are considered. The parameter of hydration number was determined by analytical analysis of quadrupole point while the molar volume of gas hydrates was calculated by using the molecular dynamics (MD) simulation technique. The initial number of moles of reacted water in current research was determined by In-situ Raman spectroscopy and results were validated against the analytical and semi-analytical rigorous model available in the open literature. The total number of moles of reacted water was calculated through a three-phase flash. In the last step of the study, High Pressure micro Differential Scanning Calorimetry (HP- μ DSC) has been used to better understand phase equilibrium and self-preservation phenomenon, and to determine the acting surface of methane

hydrate, which is a crucial parameter in methane hydrate dissociation kinetic. Finally, a new model for methane hydrate dissociation kinetics was proposed and its validity was assessed against experimental data, showing a better agreement when compared to the conventional model approach.

Keywords: Clathrate gas hydrates, second moment, molecular dynamics (MD) simulation, In-situ Raman spectroscopy and High-pressure microcalorimetry (HP- μ DSC)

RESUMO

HEIDARYAN, E. Estudo cinético da formação e dissociação de hidratos de gás. 2020. 170 p. D.Sc. Tese - Engenharia Química, Escola Politécnica, Universidade de São Paulo, São Paulo, 2020.

Em 1884 iniciou-se a corrida pela compreensão da cinética e do equilíbrio químico, com os trabalhos de Jacobus Henricus van't Hoff e Henry Louis Le Chatelier. Desde então, a investigação científica sobre a direção, a estabilidade e o equilíbrio das reações químicas não parou. O estudo do equilíbrio e a cinética de formação dos hidratos (ou clatratos) de gás, cristais contendo moléculas de gás em estruturas formadas por moléculas de água ligadas por ligações de hidrogênio, faz parte dessa grande corrida. O conhecimento preciso do equilíbrio e da cinética de formação dos hidratos de gás é vital para garantir a vazão das linhas de transporte de gás natural. Tradicionalmente, a maioria dos estudos cinéticos analisa a solução e a dissolução indicadas pelas mudanças de pressão em um sistema fechado. Nesta pesquisa, um estudo em reator padrão foi usado para avaliar a formação e dissociação de hidrato de metano a 276,2 K e várias pressões (2700, 2900 e 3200kPa). Entre os muitos parâmetros estudados, o segundo momento da distribuição de tamanho de partícula ($\mu_2(t)$) mostrou-se a chave para o entendimento do hidrato de gás produzido. O principal objetivo desta tese, portanto, foi determinar o segundo momento da distribuição de tamanho do hidrato de metano $\mu_2(t)$ com base em um modelo analítico deduzido do balanço de massa. Na construção do modelo, os parâmetros como o número de hidratação, o volume molar do hidrato de gás, a quantidade inicial de água reagida e a quantidade total de água reagida são encontrados. O parâmetro de número de hidratação foi determinado pela análise analítica do ponto de quadrupolo, enquanto o volume molar de hidratos foi calculado usando a técnica de simulação de dinâmica molecular (MD). O número inicial de moles de água reagida foi determinada por espectroscopia Raman in situ, e os resultados foram validados por modelos rigorosos (analítico e semi-analítico) disponíveis na literatura aberta. O número total de mols de água reagida foi calculado por meio de um flash trifásico. Na última etapa do estudo, micro-calorimetria diferencial de alta pressão (HP- μ DSC) foi usada para entender melhor o equilíbrio de fases e determinar a superfície ativa do hidrato de metano, parâmetro crucial na cinética de dissociação dos hidratos. Finalmente, um novo modelo de dissociação de hidrato de metano foi proposto, e sua validade foi

verificada, mostrando uma melhor concordância com os dados experimentais quando comparado à abordagem convencional.

Palavras-chave: hidratos de gás, segundo momento, simulação de dinâmica molecular (MD), espectroscopia Raman in situ e micro-calorimetria de alta pressão (HP- μ DSC)

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1 INTRODUCTION AND BACKGROUND

1.1. GAS HYDRATES, STRUCTURE, AND PROPERTIES

Gas hydrates (also known as clathrate hydrates) are crystalline compounds in which small gas molecules are trapped inside hydrogen-bonded water molecules cages, typically at high pressure and low temperature (for example, 10000 kPa, 277 K for methane hydrates) (Sloan and Koh, 2008). In total, about 60 gas species form gas hydrates, being the most commonly found in nature, those containing methane, ethane, propane, and carbon dioxide (Sloan, 2003). Figure 1.1 shows the typical structure of a gas (methane) hydrate.

Figure 1.1 - Typical structure of a gas hydrate showing water molecules linked together to form a cage that traps a gas molecule, such as methane, inside.

Source: (Maslin et al., 2003)

The three main hydrate structures identified so far are cubic structure sI, cubic structure sII, and hexagonal structure sH (Ripmeester et al., 1987). These three hydrate structures are illustrated in Figure 1.2. The cubic hydrate crystals (sI and sII) have two different cage sizes, but the hexagonal one (sH) has three different ones. One type of guest molecule is enough to stabilize the hydrate, except for sH hydrate that requires guest molecules of two different sizes. Shaped with guests having diameters between

4.2 and 6 Å, the structure I is containing molecules such as methane, ethane, carbon dioxide, and hydrogen sulfide. Tiny molecules, including hydrogen, and Nitrogen ($d < 4.2$ Å) as single guests construct structure II. Large single guest molecules such as iso-pentane or neohexane (2,2-dimethylbutane) with a typical size of $7 \text{ Å} < d < 9 \text{ Å}$ when accompanied by smaller molecules such as methane, hydrogen sulfide, or nitrogen can build structure H (Sloan and Koh, 2008).

Figure 1.2 – Hydrate structures identified so far. SI has two small cages composed of pentagons (5^{12}) of hydrogen-bonded water molecules and six large cages consisting of hexagons and pentagons ($5^{12}6^2$). In each unit cell of SII, there are 16 small cages formed of pentagons (5^{12}) and eight large cages built of hexagons and pentagons ($5^{12}6^4$). Structure H is composed of 3 pentagons (5^{12}), two $4^35^66^3$ cavities, and one $5^{12}6^8$ cavity for guest molecules.

Source: (Strobel et al., 2009)

1.1.1 Gas hydrates a nuisance, a resource or even potential technology

Solving gas hydrates issues plays a significant role in the flow assurance of oil and gas flow lines. The formation of gas hydrates in flow lines can be not only fast but also in large volumes, causing unexpected operational problems (Sloan, 2010). Figure 1.3 shows two very well-known photos regarding the conditions of oil and gas pipelines and hydrate problem.

Figure 1.3 - Temperature change as a result of pressure dropdown (Joule–Thomson effect)
 b) hydrate plug formed in an offshore gas pipeline, diameter 16 in.

Source: a) www.oilandgasteam.com b) <http://hydrates.mines.edu/>

Traditionally natural gas hydrates are considered hazards, and their formation should be avoided by getting away from their phase boundaries. The first work regarding natural gas hydrate phase behavior was attributed to Wilcox et al. (1941) who studied phase equilibrium for four alkanes and five natural gas mixtures. This work, was followed by a solid-vapor equilibrium ratio correlation proposed by Carson et al. (1942), which together with Wilcox's work, forms the backbone of engineering for understanding of natural gas hydrate behavior. These findings concluded as a natural gas hydrate chart (Figure 1.4), which is the reference graph for natural gas hydrate equilibrium (Ahmed 2018; GPSA 2017).

Figure 1.4 - Hydrate formation prediction chart.

Source: (Ahmed 2018; GPSA 2017)

From the kinetic point of view by drawing analogies with observed flow regimes in ice-water mixtures, it was proposed that these regions corresponded to three distribution states of hydrate particles, as shown schematically in Figure 1.5:

- (1) homogeneous particle distribution
- (2) heterogeneous particle distribution (in other words, variable particle concentration in the radial direction), leading to a moving bed-type accumulation
- (3) stationary bed formation and catastrophic deposition resulting in plug formation.

Figure 1.5 - A simplified conceptual picture of the formation of hydrate blockages in a pipeline.

Source: (Akhfash et al., 2003)

Around the permafrost regions and the ocean floor all over the world, vast amounts of methane gas are naturally deposited in hydrate form when the thermodynamic conditions are favorable. Such methane gas has been originated from thermogenic and biogenic bases and hydrate formation is the result of upward migration of methane gas to water regions (Kvenvolden, 1993a). The estimated content of methane gas in hydrate form is believed to be ten times more than in all the conventional gas resources at present (Kvenvolden, 1993b). Therefore, gas hydrates foretell a vital gas reserve for the upcoming (Holder et al., 1984). It is particularly imperative due to the global need to switch to a renewable energy for the future. The gas, which is cleaner than petroleum, is considered a suitable replacement energy. Thus, It would be possible to fill this need by exploiting the gas from gas hydrate reserves.

There is a lot of progressing research into understanding the foremost reasonable means of producing this ultimate energy source (Pooladi-Darvish, 2004). Discoveries from phase equilibria of gas hydrate and formation kinetics have encouraged investigation on gas hydrate based on new applied science in gas exploitation, storage, transportation, and separation. Some gas hydrate guest molecules such as carbon dioxide form more abiding hydrates than methane at the same conditions.

Consequently, carbon dioxide can replace methane gas from methane hydrate sediments. In this fashion, undesirable carbon dioxide may be stockpiled through capturing in hydrate form while synchronously exploiting methane for usage as energy (Ohgaki et al., 1996).

Ersland et al. (2010) used Magnetic Resonance Imaging (MRI) to provide evidence that in the presence of carbon dioxide a large portion of the methane hydrate was not dissociated into liquid water or ice, (at 8274 kPa while temperature never went below 276.75 K) and that only a partial fragmentation of some cage structures occurred with the exchange of methane and carbon dioxide molecules when carbon dioxide was injected into the hydrate sample. The general appliance of the methane–carbon dioxide interchange reaction is demonstrated in Figure 1.6.

As discussed, the formation and decomposition process of gas hydrates involves many industrial areas so, research on thermodynamic equilibrium and formation of dynamics is fundamental. From now on, there have many notable achievements being made and theoretical research on hydrate thermodynamics. Due to the complicated process of hydration reaction, the uncertainty of the nucleating process, as well as some underlying problems such as driving force, induction time, and growth rate, have not been solved, research on dynamics has been still in the primary stage.

Figure 1.6 - (a) Schematic illustration of the CH_4 – CO_2 exchange reaction in three steps. (b) Kinetic example of CH_4 – CO_2 exchange reaction. (Left side of red dash) CH_4 hydrate formation stage when 100% of guest molecules are CH_4 . (Right side of red dash) CH_4 – CO_2 exchange stage where ~64% of CH_4 molecules are exchanged with CO_2 molecules.

Source: (Koh et al., 2016)

Phase stabilities of gas hydrates rely on the guest molecule apprehended in the hydrate assembly. Figure 1.7 shows thermodynamic equilibrium curves for hydrates of pure methane and pure carbon dioxide, along with the saturation equilibrium line of carbon dioxide (Koh et al., 2016).

The phase boundary for pure hydrate of carbon dioxide has both lower and upper quadruple points (only upper quadruple point of CO_2 is shown in this figure, in which liquid water, hydrate, vapor CO_2 and liquid CO_2 are in equilibrium). In contrast, hydrate of pure methane has only one quadruple point, in which liquid water, hydrate, ice and methane gas are in equilibrium and it is shorn of an upper quadruple point, since the quadruple point of methane is higher than the critical point of it (4700 kPa and 190.5 K).

Figure 1.7 - Thermodynamic phase equilibria curves for pure CH_4 and pure CO_2 hydrates, along with phase equilibrium lines of liquid and gaseous CO_2 .

Source: (Koh et al., 2016)

When the equilibrium conditions of hydrate formation from gaseous CO_2 ($H-L_w-V_{\text{CO}_2}$) and CH_4 are compared, it is observed that hydrates of pure carbon dioxide assemble at higher temperatures than pure methane hydrates at a given pressure. Likewise, pure carbon dioxide hydrates from gaseous carbon dioxide form at a lower pressure at a given temperature. When the position of the upper quadruple point is below the

pressure of liquid carbon dioxide, the phase boundary of the carbon dioxide hydrate exhibits a sharp slant and crosses with the curve of the methane hydrate (Seo; Lee, 2001).

For both gas hydrates, the overall thermodynamics evaluations disclose that pure carbon dioxide hydrates have moderate formation conditions than pure methane hydrates when gaseous carbon dioxide is present. By way of explanation, even though temperature and pressure conditions may not be proper to form pure methane hydrates, or, pure methane hydrates are so insecure that they decompose at a given pressure and temperature condition, carbon dioxide can still react with water to produce pure carbon dioxide hydrates, and liquid carbon dioxide can show a responsive propensity up to convinced conditions.

1.1.2 Hydrate Formation Kinetics

The kinetics of formation and decomposition of gas hydrates is an essential area of hydrates research. Vysniauskas and Bishnoi (1983; 1985) used an Arrhenius-type equation empirically as a rate equation formula of

$$r = Aa_s \exp\left(-\frac{\Delta E_a}{RT}\right) \exp\left(-\frac{a}{\Delta T^b}\right) P^\gamma \quad (1.1)$$

Here the controlling mechanism is the reaction kinetics. In this formula, r represents the consumption rate of gas during hydrate formation; A is lumped pre-exponential constant, a_s is the effective surface area of the gas-water interface, ΔE_a is apparent energy of activation for hydrate formation, R is the universal gas constant, T is temperature, a and b are empirical parameters, P is pressure and γ is the overall order of the reaction. In the above equation, ΔT represents the degree of supercooling, which is equal to the difference between the experimental temperature and the hydrate-liquid water-gas gas equilibrium temperature corresponding to the experimental pressure. Although all of the parameters in this model are well defined, their measurement is not easy. For example, measurement of the effective surface area of the gas-water interface is associated by a high order of uncertainty (Vysniauskas; Bishnoi, 1983) so, for reliable performance, five parameters (A , ΔE_a , a , b , and γ) of the current model are needed to be fitting to experimental data.

In 1987 Englezos and co-workers considered spherical particles, they presumed that the inside surface of the surrounding layer is equal to the outside one, which is the surface of the particle and planned the first kinetic model (Englezos et al., 1987a and b) as:

$$\frac{dn}{dt} = KA_p (f - f_{eq}) \quad (1.2)$$

Where K is the only adjustable parameter (the overall kinetic rate constant) for the formation of methane and ethane gas hydrates in this model. Mass transfer is the controlling mechanism and the fugacity difference of gas-phase with the population balance model act as a driving force. The A_p in this formula is hydrate particle surface area, and f is the fugacity of guest gas. The subscript of eq refers to equilibrium. Their work provided a comprehensive base for the explanation of gas hydrate formation kinetics by means of crystallization concept united with the mass transfer phenomena at the gas-liquid interface.

Reviewing available models in the open literature Yin et al. (2018) came up that most of the model's formulation massively hinge on the conformations of the reactor of hydrate, the contact ornament of the multiphase fluids (gas-liquid-hydrate, liquid-liquid-hydrate) and the techniques of gas hydrate formation not resulting from primary principles. It also should be considered that there is no undeviating model that could explain for all the practical hydrate grow kinetic behavior up to now.

The nature of the hydrate formation process is more physical rather than chemical. It starts when a guest comes in contact with a host under suitable pressure and temperature. Therefore, at specific conditions of pressure and temperature in the hydrating domain of the partial-phase diagram, the time required to begin forming hydrate crystals (induction time) and the rate of growth of hydrate crystals are two-time dependent fundamental factors that should be considered in hydrate kinetic studies (Englezos, 1993). Nucleation and growth may be overwhelmed by many issues, such as subcooling, pressure, temperature, previous history of water, composition, and state of the gas hydrate forming system (Makogon et al., 2000).

The emblematic use of gas during gas hydrate formation is showed in Figure 1.8 in which nucleation (region 1) and growth (regions 2 and 3) are two major stages of the process of hydrate formation.

All these factors limit the experimental research activities of hydrate formation kinetics. In the following sections, these two stages will be discussed.

Figure 1.8 - Typical gas uptake curve during gas hydrate formation.

Source: (Yin et al., 2018)

1.1.3 Nucleation of Gas Hydrates

The nucleation of gas hydrate is a phenomenon in the microscopic level in which gas and small clusters of water (hydrate nuclei) raise and scatter to reach critical size for continuing crystal growth (Sloan; Koh, 2008). On the whole, the nucleation is a complicated and stochastic process, particularly previously attainment a steady-state regime, where steady-state nucleation occurs, which predicts hydrate onset unlikely (Kelton et al., 1983; Kelton et al., 1996; Koh et al., 2011).

Studies on the mechanism of hydrate nucleation started decades ago. The first mechanism proposed for the hydrate nucleation process introduced a new parameter: the guest/cavity size ratio (Sloan; Fleyfel, 1991). The hypothesized mechanism consisted of a series of consecutive reactions, progressing from the stable species (ice, gas and liquid water film) to the formation of labile species within the liquid film at the ice interface and finally to the beginning of crystal monotonic growth species with

the attainment of a critical hydrate radius. This hypothesis was verified based on only two reproducible sets of kinetic data available at the time for gas hydrate formation from an agitated ice surface. However, it proposed a means of guiding experiments for the next refinements and corrections.

Later, an extended mechanism was proposed by Christiansen and Sloan (1994) for the kinetics of hydrate formation. The proposed mechanism was composed of two parts:

- (1) the construction of bunches of hydrogen-bonded water molecules around guest molecules
- (2) the construction of these bunches (or clusters) to form a hydrate nucleate.

This mechanism called the “labile cluster” hypothesis is one of the two main hypotheses suggested for hydrate nucleation. The other hypothesis is “local structuring,” proposed by Radhakrishnan and Trout (2002). In the labile cluster hypothesis, liquid water molecules are gathering around a dissolved solute molecule in a “pre-hydrate” structure, with basically the precise harmonization number. In contrast, in the local structuring hypothesis, the “pre-hydrate” structure involves a locally well-organized water-guest assembly rather than discrete hydrate cavities.

The natural gas hydrates formation starts with a heterogeneous or homogeneous nucleation incident (Anderson et al., 2005). In the homogeneous nucleation, hydrate creation occurs in a single-phase consist of no impurities. In the heterogeneous nucleation, hydrate formation transpires in the presence of two or more phases, and/or impurities, which attend as nucleation catalysts.

Figure 1.9 illustrates the conceptual model that has been proposed for hydrate nucleation (Sloan; Koh, 2008). Further research to validate these hypotheses were focused on Molecular Dynamics simulation rather than experiments because of both their stochastic and microscopic manner and the timescale resolution of most experimental techniques (Sloan; Koh, 2008).

Analyzing the free energy surface leads to determining the critical cluster size that causes the nucleation of the clathrate phase. In a molecular dynamics simulations of CO₂ hydrate clathrates, Radhakrishnan and Trout (2002) concluded for CO₂, a thermal fluctuation causing the local ordering of molecules leads to the nucleation of the

clathrate that the nucleation proceeds via “the local structuring mechanism,” leads to the nucleation of the clathrate, and not by the current conceptual picture, called “the labile cluster hypothesis.”

Figure 1.9 - A conceptual model of hydrate nucleation at the liquid-gas interface.

Source: (Sloan; Koh, 2008)

The former molecules local ordering makes the collation of the water molecules at the nearest- and next-to-nearest-neighbor shells, which are taken by a three-body host–host order parameter, ζ^{hh} ; these thermodynamic fluctuations lead to the creation of the critical nucleus.

1.1.4 Growth

When the hydrate growth and amalgamation of the crystals occur, it leads to the formation of a solid mass. Growth processes are swift reactions, especially during the early growth periods. A theoretical representation for crystal growth united with either the labile cluster or local structuring hypotheses for nucleation is projected and described in the literature (Sloan and Koh, 2008). During the growth process, mass and heat transfer and the nucleation parameters, including displacement from equilibrium conditions, surface area, agitation, water history, and gas composition, become of major importance. In the proposed picture of hydrate growth, a combination of three factors have been considered (Sloan and Koh, 2008):

- (1) The crystal growth kinetics at the surface of hydrate
- (2) Compounds mass transfer to the increasing crystal surface
- (3) Hydrate formation exothermic heat away from the increasing surface of the crystal

For a multi-component system containing different chemical additives, such coupled heat and mass transfer is a complex process, and its explanation in a mathematical way is thorny. Also, studying the kinetics of hydrate nucleation and modeling of hydrate growth requires a lot of experiments to be performed. However, only restricted quantities of correct data are available for crystal growth rate after nucleation.

Unlike the stochastic hydrate nucleation process, the hydrate growth rate can be quantified, which increases the chance of developing more hydrate formation models (Abay, 2011).

Quantification and analysis of experimental hydrate growth data are mostly implemented using a simple but powerful method. In the constant-volume hydrate procedure, hydrate growth leads to a pressure drop. It can give an estimation of the number of hydrates formed in the liquid phase. The number of moles of gas consumed (Δn) until time t for single component hydrate crystallization in the solution is an experimentally accessible quantity, which is related to the gas pressure drop in the system.

$$\Delta n = \left(\frac{PV}{ZRT} \right)_0 - \left(\frac{PV}{ZRT} \right)_t \quad (1.3)$$

P , V , and T are the pressure, volume, and temperature of the guest gas, respectively. R is the gas universal constant, and Z is the compressibility factor obtained by an equation of state (EOS). To calculate the number of gas moles converted to gas hydrates, it is necessary to consider the fact that the guest gas is soluble in water.

To be able to find the number of moles of gas that have been converted to hydrates, the fact is using that the mole fraction of the gas hydrate former in the bulk liquid phase at the onset of hydrate growth and thereafter does not change significantly with time (Bergeron and Servio, 2009). This can give an estimation of some hydrates formed in the liquid phase.

The hypothesis of hydrate growth as a crystal may be associated with either the labile cluster or local organizing theories for nucleation and it is publicized in Figure 1.10.

Figure 1.10 - A conceptual model of hydrate crystal growth where a guest molecule (black circles) restricted by a cluster of unstable water (grey circles) adsorbs to the film of growing hydrate; as the guest molecule is combined into cage network of the growing, molecules of water are able to spread back into the aqueous phase.

Source: (Sloan; Koh, 2009)

Imagine the bunch is restrained in three dimensions (vii, which not shown). At (ii), (iv), (vi) the cluster is united into the crystal surface, it is entered proper cavity, and extra solvent molecules are unconfined. At (i), due to the lower Gibbs free energy bring at the crystal surface, the cluster is driven to the surface (growing crystal surface). (iii) As the solid force field is perpendicular to the crystal face, the cluster diffuses (only in two dimensions) over the surface to a step in the crystal. (v) The cluster disperses along the step to a bend or blemish in the step (as it can now move only in a single dimension).

Theatrically polycrystalline growth and crystallization of gas hydrate depend on an extension of the theory of phase-field, which is based on the orientation field (θ), first introduced by Kobayashi al. (1998). This field distinguishes the crystal planes local orientation in the experimental system and permits the explanation of grain boundary evolution and polycrystalline solidification.

The field of orientation is massively synchronized to the phase-field so that orientational and structural variations occur concurrently at the interface of crystal-liquid.

This coupling is understood by count an orientational influence to the functional of free energy.

$$F = \int d^3r \left(\frac{1}{2} \varepsilon^2 T (\nabla m)^2 + f(m, c) + f_{ori}(m, \nabla \theta) \right) \quad (1.4)$$

In which

$$f_{ori}(m, \nabla \theta) = (1 - p(m)) HT |\nabla \theta| \quad (1.5)$$

is the driving force for orientational ordering, and H is a constant.

From an experimental point of view, the suggested concept of driving force can be expressed as in Figure 1.11, where x_{int} shows the interfacial mole fraction of the hydrate former (gas) at given pressure and temperature and x_{int}^{eq} is the interfacial mole fraction of the hydrate former at equilibrium conditions (equilibrium pressure and temperature) of hydrate formation.

Source: (Khosharay et al. 2015)

It can be seen in Figure 1.11 that for each operating condition, the interfacial mole fraction of the hydrate former (x_{int}) is calculated for two points: The first point contains the operating temperature (T) and pressure (P_i). The second point includes the working pressure (P_i) and the temperature corresponding to the equilibrium temperature for operating pressure (T_{eq}). In the literature (Kamath al. 1987; Freer al. 2001),

temperature differences between bulk fluid and hydrate phases have been assumed to be a single driving force.

1.2. HARDWARE AND SOFTWARE USED IN DETERMINATION OF KINETIC OF GAS HYDRATES

Two different sets of experimental setups have been used in this study. The first set was a conventional high-pressure cell equipped with pressure and temperature control and recording, which was used for the hydrate formation and dissociation study. It is entirely normal to use time-dependent Raman spectroscopic measurements to provide data on formation or dissociation processes such as the methane transformation from the water phase to the hydrate phase (Subramanian; Sloan, 1999). This setup also was equipped with two in-situ Raman spectroscopic probes. This equipment has been used to study and obtain vital information regarding gas solubility, the structure of the hydrate, hydrate composition, and cage occupancies. Raman spectra are also used in this work to measure the solubility of guest gas in water in the presence of gas hydrate.

The experimental method which has been used in this study to monitor thermal behavior of gas hydrates was the High-Pressure Differential Scanning Calorimetry (HP- μ DSC). Using the advantage of shorter analysis time, simple experimental procedure, and a smaller amount of required material, the HP- μ DSC is using for determining equilibrium data and also for obtaining other thermal properties such as enthalpy and heat capacity (Dalmazzone et al., 2002; Parlouër et al., 2004; Gupta et al., 2008). On the one hand, since the hydrate layer is formed in the interface of gas and liquid phases, and because of the absence of mixing in most of HP- μ DSC configurations, hydrate growth inside the cell may undergo mass transfer issues. The use of in-situ agitation in the mentioned setup is limited by the difficulty of installing a small size but powerful motor drive system coupled to an internal stirrer located inside the HP- μ DSC cells, that should be able to withstand high pressures without leaks. In addition, the energy induced to the sample by in-situ stirring can make the temperature control more difficult.

On the other hand, the HP-microcalorimeter allows operating at two different modes: isobaric and isochoric. When using the isobaric approach for the thermal scanning, it would be possible to determine the number of moles of gas consumed to form the

hydrate from the volume of gas inserted into the system or removed from it to maintain constant pressure. A linear trend is expected when representing volume of gas versus temperature of the sample in the cell, but an abrupt change should be observed during hydrate formation or dissociation due to the phase change. However, the commercial HP-microcalorimeter does not include the option for recording this volume change and this characteristic must be customized and has not been already tested. Isochoric mode would make possible to detect tiny changes of pressure, but since the pressure sensor is located in the gas panel, not inside the calorimetric cells, once the panel chamber is closed to work at constant volume (referring to the volume of the cell plus the volume of the tube connecting the gas panel to the cells), it is not possible to relate pressure drop or pressure build-up to the amount of gas dissolved in the water sample.

These limitations caused kinetic studies that are carried out in the HP- μ DSC system to be reduced to study inhibitors' performance of different systems. For example, Daraboina et al. (2011), by using a μ DSC system, investigated the effect of kinetic inhibitors of both chemical (PVP and H1W85281) and biological (type III antifreeze protein) nature, on natural gas hydrate formation. In another study, Farhadian et al. (2019) used the μ DSC system to evaluate the methane hydrate melting curves in the presence or absence of waterborne poly urea/urethanes (WPUUs) using the temperature ramping protocol. In this study, a HP- μ DSC evo, Setaram Inc., is used for calorimetric studies to determine methane hydrate equilibrium temperature and enthalpy of the dissociation process at high pressures.

The knowledge of simulation of the time-dependent behavior of a system of particles is called as molecular dynamics. A definition of a simple molecular dynamics (MD) simulation consists of considering atoms integrating the equation of motion with appropriate boundary conditions for the shape and geometry or symmetry of the system followed by true time evolution. MD is returning data at microscopic level, that is: atomic velocities and positions. To compute a microscopic behavior of a system through the classical mechanics laws, MD needs, as an input, an explanation of the interaction potential (or force field). So, the value of the results of an MD simulation stalwartly depends on the precision of the explanation of the inter-particle interaction potential. Thus, the MD technique acts as a computational microscope. Through using statistical mechanics, these microscopic data are then transformed to macroscopic properties like pressure, temperature, heat capacity, stress tensor, and so on. The

molecular dynamics method was extensively applied by almost all the branches of knowledge, such as determining of rates of chemical reactions, evaluation of solid-state structures, defects and surfaces formation in material science, folding of protein in biochemistry, and many other fields. Currently, Wei et al. (2018) studied multi-nodes of temperatures and pressures, microscopic decomposition mechanisms of structure I methane hydrate in contact with bulk water molecules by using molecular dynamics simulation. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a molecular dynamics program from Sandia National Laboratories. In this research, LAMMPS has been used for calculating the molar volume of gas hydrates.

1.3. MOTIVATION AND DISSERTATION OBJECTIVES

Although Hammerschmidt (1939) published the first paper on gas hydrate as an issue in natural gas pipelines, it was not considered a severe point until the 1960s, because in that era it was usual to burn natural gas in oilfields as an undesired side product. However, by increasing oil prices, natural gas turned to be an asset, and many researches were carried out on natural gas hydrate, being the main focus the time-independent evaluation of gas hydrate properties (Holder et al. 1980). This focus changed and since the mid-1980s, kinetic behavior of hydrate formation and decomposition (Vysniauskas and Bishnoi, 1983; Englezos et al., 1987a; Kim et al., 1987), was considered as the most interesting and fascinating process (Sloan and Koh, 2008).

The kinetic reasoning of gas hydrate formation is much more complex than gas hydrate dissociation in comparison (Yin et al., 2016) as hydrate formation involves two joined procedures: the stochastic hydrate nucleation process and the hydrate growth process (Sloan and Koh, 2008). It is a broad subject since, at times, multiscale, it needs an examination of compounds dispersion in multiphase under numerous liquid-gas contact paradigm.

A glance into the literature reveals that the fundamental understanding, that precisely defines the gas hydrate formation behavior fundamental knowledge, qualified the basis of the governing equations. A thorough thoughtful of hydrate formation behavior requires insight of thermodynamics (Seo et al., 2019), heat and mass transport phenomena, colloid science (Xin et al., 2019), reaction engineering (Tian et al., 2017), multiphase fluids flow and flowlines (Tang et al., 2016) in addition to mathematical

modeling (Hashemi et al., 2007; Zerpa et al., 2013), as well as numerical simulation and methods (Li et al., 2018), since results need to be reported quantitatively.

A proper hydrate formation kinetics understanding may be beneficial for three key explanations:

(i) to upsurge the amount of gas hydrate formation, which is dangerous in most hydrate-associated technologies, for example, hydrate-based gas storage (Jarrahian; Heidaryan, 2014) hydrate-based gas capture and, sequestration (Babu et al., 2013; Babu et al., 2015; Dashti et al., 2015);

(ii) to decrease the proportion of gas hydrate creation, which is helpful in hydrate risk management and inhibition in the field of flow assurance (Lederhos et al., 1996; Heidaryan et al., 2010);

(iii) to understand the place and amount of formation for naturally occurring gas hydrates in a marine or permafrost locations of the geological environment (Clennell et al., 1999; Klauda et al., 2005) or even in energy production from hydrate site (Deusner et al., 2012).

The gas hydrate growth investigation was almost happening from workroom tests, where gas hydrates were formed inside a high-pressure reactor with formation rate measured (Vysniauskas; Bishnoi, 1983; Englezos et al., 1987a; Englezos et al., 1987b) with regard to the pressure decline. Subsequently, kinetic models were expressed to capture the physical behavior of the system, although considering some simplification assumptions. Since validation of model results against experimental data is vital, the answer to the governing equations in the planned model was gained. Limitation and application analysis of model performance has also been discussed in the literature (Englezos et al., 1987a; Skovborg; Rasmussen, 1994; Mori, 1998). With the progress in the computing ability and instrumentation over the past decades, models planned and faced additional improvements by mingling newly experiential phenomena, more erudite physics, better-calculated constraints, or more noteworthy solution methods. However, regularly semi-empirical constants in the kinetic models need to be fitted because of the absence of knowledge and insight into the problem. One of these parameters is the (K) or kinetic rate constant which may be formulated as an overall reaction rate for all the particles (in other words summing the rate per particle for all particles of different size) as result of the 4π multiplied by second moment of the

particle size distribution ($\mu_2(t)$) and multiplied by combined rate parameter (K^*). Measurement of $\mu_2(t)$ in literature is limited to a minimal number of published works (Bergeron and Servio, 2008a; Bergeron and Servio, 2008b; Bergeron et al., 2010) for a few different guest gases.

Thus, the main objective of this work is to review fundamentals of the gas hydrate kinetic, have an insight into the physics behind the phenomena, and determine a way to obtain a model through available measurable parameters to reproduce the kinetic behavior of gas hydrates. Thus, this work contributes to not only scientific fundamentals but also tries to provide a vision into the application in this area.

1.4. OUTLINE OF THE WORK

This dissertation is composed of seven chapters written according to the motivation mentioned above. To this end, as the first chapter, it has been dealing with the scientific context and the primary references found in the literature related to this topic.

Chapter 2 corresponds to the description of the kinetics of gas hydrate formation while it is digging the open literature to provide reasonable relation between physics, forces, and potentials as well as link them to the measurable parameters.

Chapter 3 deals with the definition of the ideal hydrates particle size distribution second moment and its origin. An analytical expression for the $\mu_2(t)$ is also proposed.

In Chapter 4 the hydration number is studied through the evaluation of enthalpy of dissociation at quadrupole points in the first part. In the second part of this chapter, the molar volume of methane hydrate simulated using MD and analytically represented in a mathematical formula is used.

Chapter 5 contains conventional studies of methane hydrate formation and validation of the proposed method for the $\mu_2(t)$. In this chapter, the solubility of methane in water and in the presence of hydrate are modeled through two-phase and three-phase flash.

Chapter 6 tries to use HP- μ DSC to evaluate hydrate dissociation temperature and enthalpy of dissociation. In contrast, the results have been used to assess the induced effects of hydrate as a curvature, which caused self-preservation in the temperatures

above quadrupole point. Finally, by applying the results of HP- μ DSC, a new model for methane hydrate dissociation is proposed.

Chapter 7 contains some key findings of this work and the general conclusion and suggestions for further investigations.

The graphical overview of this study is reflected in Figure 1.12.

Figure 2.12- The graphical overview of this study.

Nomenclature

A	lumped pre-exponential constant
a	empirical parameter
a_s	effective surface area of the gas-water interface
b	empirical parameter
f	fugacity of gas at gas state
K	overall kinetic rate constant
P	pressure
R	universal gas constant
r	consumption rate of gas during hydrate formation
T	temperature
x_{eq}^{int}	interfacial mole fraction of the hydrate former at equilibrium conditions
x^{int}	interfacial mole fraction of the hydrate former
Z	compressibility factor
γ	overall order of the reaction
ΔE_a	apparent energy of activation for hydrate formation

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2 LITERATURE REVIEW ON KINETICS OF GAS HYDRATES

2.1. NUCLEATION OF GAS HYDRATES

The formation of a gas hydrate phase includes two significant stages of (i) nucleation, which is the advent of unchanging nuclei of a new phase and (ii) their growth. Considering the theory of classical nucleation, having a stable phase in a bulk metastable phase (here is dissolved guest gas in water) requires the formation of a nucleus (a small particle) of the stable phase capable of growing spontaneously. The nucleation from liquid water to form gas hydrate arises most often close to the gas-liquid interface (Englezos et al., 1990; Ribeiro and Lage, 2008; Sloan and Koh, 2008).

Boewer et al. (2012) examined the construction of these interfaces under sluggish circumstances in situ by means of X-ray reflectivity measurements both inside and outside the zone of hydrate stability. They concluded that the maximum supersaturation of the liquid with soluble gas and the highest concentration of water vapor in the gas phase occurs in this district. The presence of a guest-enriched film at the interfaces of water-carbon dioxide and water-xenon was confirmed, but such film was not originated in the systems formed by water-propane and water-isobutane. Sufficient supersaturation of the guest gas in the solution also will cause the nucleation of the hydrate in the bulk of the liquid phase not to be streaked.

The water structures and aqueous solutions of hydrophobic components are strongly connected with the concept of hydrate nucleation. Nilsson and Pettersson (2011), by scattering data of X-ray absorption spectroscopy, declared that the water molecules are mostly in the 3D network of hydrogen bonds of the liquid phase, which are involved in the chunk of snap formations of these bonds and have a character in common with constructions of ice. These configurations are very swiftly interchanged as a result of the rotational and translational fluctuation of water molecules. Interestingly Brovchenko et al. (2005), using Monte Carlo (MC) simulations, showed that increasing temperature and pressure cause a decrease in the structuring of liquid water.

From the chemical point of view, molecules of water are not able to form bonds with molecules of guest gas, which leads to local interruption of the network of the hydrogen bond. As this happens, water molecules reorganize and create a kind of enclosure around the gas molecule, the internal surface of the cage is lined up by hydrogen bonds of water molecules, which are mainly oriented tangentially to the hydrophobic molecule

surface (Filipponi et al., 1997; Koh et al., 2000; Buchanan et al., 2005). The resulting cage will cause cavities that lead to the initiation of clathrate hydrates (Figure 2.1. shows this concept).

Figure 2.1 - Adsorption of the guest gas molecule onto labile hydrate cavities at the gas-water interface.

Source: (Sloan; Koh, 2008)

These agglomerated cavities are constructing elements of the hydrate frame. As the temperature declines, they branch together in the adjacency of the gas-liquid boundary and act as hydrate precursors. At this step, nano-sized entities containing from tens to hundreds of unit cells are forming the nucleus of the nascent phase.

To represent hydrate formation through classical nucleation theory, Kashchiev and Firoozabadi (2002; 2003) described hydrate formation through a combination of analogous building units and assumed the work required for the establishment of a nucleus containing n building units as

$$W(n) = -n\Delta\mu + c\sigma_{ef}(V_h n)^{2/3} \quad (2.1)$$

Where W is the work required for the creation of a nucleus containing n building units in Joule; $\Delta\mu$ is the gain of the volume free energy change of one building unit from the phase of supercooled to the hydrate in Joule; c is the shape factor characterizing the geometry of the nucleus (for a spherical cluster is shaped in homogeneous nucleation, $c = \sqrt[3]{36\pi}$); σ_{ef} is the effectual peculiar surface energy of the nucleus in $\text{Joule}\cdot\text{m}^{-2}$ and

V_h is the volume of a unit in m^3 . The first term in the equation exemplifies the volume energy, and the second term symbolizes the surface energy of the nucleus.

It is also reasonable to consider hydrate nucleus shaped like a sphere and considering the relation between work and energy, representing Equation (2.1) in terms of particle radius (r) and excess Gibbs free energy (ΔG) as:

$$\Delta G = \Delta G_v + \Delta G_s = \frac{4}{3}\pi r^3 \Delta g_v + 4\pi r^2 \sigma \quad (2.2)$$

In this form, ΔG_v is the volume excess Gibbs free energy, ΔG_s is the surface excess Gibbs free energy, and ΔG equals to the sum of them. Δg_v is the free energy change per unit volume.

Figure 2.2 shows the shape of the curve, illustrating the dependence of the nucleus energy on the number of building units.

Figure 2.2 - Work done to form the gas hydrate nucleus against the number of building units in the nucleus.

In Equation 2.1, hydrate formation driving force is elected as $\Delta\mu > 0$. For an isothermal process, the specific terminologies for the driving force of hydrate formation (Englezos et al., 1987) is express as:

$$\Delta\mu = k_B T \ln \frac{f}{f_{eq}} + \Delta V_e (P - P_{eq}) \quad (2.3)$$

Where k_B is the Boltzmann constant; T is hydrate formation temperature; f and P are the fugacity and pressure of the hydrate-forming while eq subscript denotes equilibrium state; ΔV_e is the variance from the volumes of water molecules in the solution and the hydrate building unit in the hydrate crystal in m^3 .

For an isobaric process, the driving force of hydrate formation is described as:

$$\Delta\mu = \Delta S_e \Delta T \quad (2.4)$$

Where ΔS_e is entropy change upon hydrate formation, and ΔT is the supercooling.

In Equation (2.1), the value of the σ_{ef} hinge on the nucleus position. The whole nucleus arises in the bulk of the liquid, in the event of homogeneous nucleation and so $\sigma_{ef} = \sigma$ (where σ is the definite superficial energy of the hydrate/liquid boundary) whereas if the nucleation process is heterogeneous, $\sigma_{ef} = \Psi\sigma$, where the coefficient Ψ can change from 0 to 1 contingent on the proportion of the definite surface energies of the interfaces among interfaces (hydrate/liquid, hydrate/solid, solid/liquid). The coefficient Ψ sizes up of the reduction in the energy of the nucleus surface, beginning with interaction with the surface of the solid particle.

Considering the industrial environment, it is usual to assume that heterogeneous nucleation occurs in the surface fluid and in the interface of container or pipe wall or even in the presence of a foreign body like dust microparticles.

So, for a hydrate nucleus shaped at the boundary among an aqueous solution of a gas and a plane surface of a solid particle shaped like a spherical piece, coefficient Ψ is defined as:

$$\Psi = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (2.5)$$

Where θ stands for the contact angle, which changes in the range $0 \leq \theta \leq 180^\circ$, it tracks from Young's equation that $\cos(\theta) = (\sigma_{s/L} - \sigma_{h/s}) / \sigma$ (here $\sigma_{s/L}$ and $\sigma_{h/s}$ are definite surface energies of the solid/liquid and hydrate/solid interfaces, respectively).

The nucleus of hydrate may contact the solid surface as hydrate can wet the surface, considering the free energy of the interface boundary between the solid particle and the hydrate is lower than the hydrate/liquid surface energy. The angle of θ describing

the gradation of wetting and, hereafter, of the reduction in the specific surface energy of the nucleus.

When $\theta=0^\circ$, then $\Psi=0$, in other words, the surface energy is not contributing anymore to the nucleus free energy. Once $\theta=180^\circ$, then $\Psi=1$ (it means that hydrate is wetting all the surface), it is more favorable for the hydrate to be formed in the bulk of liquid, and predominates homogeneous nucleation (HON). Hence, the smaller the angle of θ , the more likely the heterogeneous nucleation (HEN).

Now it is possible to define the maximum work required for the creation of a nucleus containing n building units with the coordinate of n^* and W^* in the $W(n)$ plot shown in Figure 2.2. The number of structural units in the alleged critical nucleus (n^*) that controls the nucleus size is described as:

$$n^* = \frac{8c^3\sigma_{ef}^3V_h^2}{27\Delta\mu^3} \quad (2.6)$$

And the work done to construct the critical nucleus (W^*), or the hydrate formation activation energy follows equation 2.7:

$$W^* = \frac{4c^3\sigma_{ef}^3V_h^2}{27\Delta\mu^2} \quad (2.7)$$

A closer look into Figure 2.2 reveals that if the number of building units (nucleus size) n is lower than n^* , a rise in the number of building units in the nucleus leads to an increase of the free energy of the nucleus. This course is unfavorable from the energy point of view, so it is more positive for the nucleus to melt. Though, if $n>n^*$, due to a decrease in the free energy, the nucleus can further growth spontaneously. Nevertheless, the hydrate nucleus seems over a random aggregation of several building units in the opening solution. The strong dependency of n^* and W^* (Equations 2.6 and 2.7) are clear on σ_{ef} and $\Delta\mu$. The creation of a nucleus as a consequence of reducing W^* can be justified because a nucleus surface interacts with the impurity's active sites, the nucleus surface energy declines, and it facilitates the process. When $\Delta\mu$ increases, a similar effect is observed. Estimations of Knott et al. (2012) showed that a crystalline nucleus containing about one hundred and fifty guest molecules and doing W^* around seventy $k_B T$ will cause homogeneous hydrate nucleation, while lower values have resulted in heterogeneous nucleation.

Jiang and ter Horst (2011) considered that the average number of nuclei N formed in a time interval t and in a volume V is related to the stationary nucleation rate J :

$$N = J V t \quad (2.8)$$

Here the J is a crucial characteristic of nucleation.

Hydrate nuclei can be formed both at the boundary and on the nucleation sites in the system (several parallel processes of nucleation), so the rate of nucleation is the sum of the rates of all involved courses. Anyway, the number of nuclei can be calculated using statistical entropy.

As the result of the product of a thermodynamics barrier and a kinetic barrier given by the rate of atomic attachment, Kashchiev and Firoozabadi (2002) assumed the nucleation of hydrates from an aqueous solution of the hydrate-forming gas. Deprived of seeing the rather cumbersome mathematical model as

$$J = A \times \exp\left(\frac{\Delta\mu}{k_B T}\right) \exp\left(\frac{-4c^3 \sigma_{ef}^3 V_h^2}{27 k_B T \Delta\mu^2}\right) \quad (2.9)$$

In which A is a parameter dependent on the mechanism of attachment of building units to the nucleus. In the case of hydrate formation in the bulk phase, it is $\text{m}^{-3} \cdot \text{s}^{-1}$, and in the case of hydrate formation on the surface, it is $\text{m}^{-2} \cdot \text{s}^{-1}$. In this formula, it is interesting that as the degree of undercooling increases, the thermodynamics driving force increases, but atomic mobility decreases.

Whether the nucleation happens under isothermal conditions, Equation (2.9) may be inscribed in the form

$$J = A \times S \times \exp\left(\frac{-4c^3 \sigma_{ef}^3 V_h^2}{27 (k_B T)^3 \ln^2(S)}\right) \quad (2.10)$$

Where,

$$S = \frac{f}{f_{eq}} \exp\left(\frac{\Delta V_e (P - P_{eq})}{k_B T}\right) \quad (2.11)$$

And for the isobaric nucleation, it trails from Equation (2.9) that

$$J = A \exp\left(\frac{\Delta S_e \Delta T}{k_B T}\right) \exp\left(\frac{-B}{T \Delta T^2}\right) \quad (2.12)$$

In which

$$B = \frac{4c^3 \sigma_{ef}^3 V_h^2}{27k_B \Delta S_e^2} \quad (2.13)$$

Even though the parameters are different in these situations of HON and HEN, it is interesting that these expressions are applicable to both.

Figure 2.3 - Methane hydrate nucleation rates in the homogeneous and heterogeneous ($\theta=90^\circ$ and 60°) nucleation (a) at $T=273.2$ K and various pressures (Equation (2.10)) (b) at $P=19.4$ MPa and various temperatures (Equation (2.12)).

Considering the spherical segment shaped the methane hydrate nucleation rate in the case of the homogeneous and heterogeneous nucleus is plotted as a function of pressure and temperature in Figure 2.3. The calculations values returned by Equation (2.10) for isothermal and by Equation (2.12) for isobaric conditions. It can be understood that in both forms, the rate is more significant for heterogeneous nucleation than for homogeneous nucleation.

There are brink numbers for the pressure rise above the equilibrium value

$$\Delta P = P - P_{eq} \quad (2.14)$$

and for the supercooling

$$\Delta T = T - T_{eq} \quad (2.15)$$

Underneath these values, the nucleation rate turns into very low; that is, nucleation of the hydrate is a rare event under these circumstances. By the rise in ΔP or ΔT in a specific array, the nucleation rate rises very quickly, and, afterward, its leftovers constant.

The survival curves or nucleation curves method (Ohmura et al., 2003) normally demonstrate the stochastic temperament of nucleation. This method presents the ratio of specimens in which the hydrate has not formed (survival curves) or has lined up (nucleation curves) by a specific point in time versus the time of supercooling (or degree of supercooling). An instance of experimental survival curves is visualized in Figure 2.4. In this figure symbols representing experimental data (Ohmura et al., 2003) describing the hydrate formation of hydrochlorofluorocarbons at various temperatures while the solid line is the result of a model which is calculating Laplace transform of the probability density of samples relevant to the spectrum of the nucleation rate.

The attained survival curve is recognized to denote to the same bunch of nucleation sites happening in the system. However, in studying nucleation, more than a few researches with one and the same sample were carried out. If the spacemen are demolished or significantly vagaries throughout the study, tests are recurrent using samples set additionally. Hereon, it is convenient to apply setups with a lot of reactors (Lee et al., 2013). The tender of approaches of this type to gas hydrate forming was ongoing rather recently (Maeda et al., 2012; Wilson et al., 2005).

Figure 2.4 - Survival curves describing the hydrochlorofluorocarbons hydrate formation at various temperatures.

Source: experimental data from (Ohmura et al., 2003)

The survival function acquired in an isothermal, isobaric test is reliably linked to the nucleation rate intrinsic in a specified system (Sear, 2014):

$$\ln \frac{N}{N_0} = -Jq(t - t_0) \quad (2.16)$$

In which N is the number of specimens in that no nuclei have been formed by time point t ; N_0 is the total number of specimens; t_0 stands for the time (s) during which the temperature grasps the definite value (the process dead time). And q stands for the volume of the liquid in the sample for bulk nucleation, or the liquid-gas contact area for surface nucleation, or the area of heterogeneous nucleation sites contemporary in the system.

For a sample chilled at a fixed rate (Stoporev et al., 2016):

$$\ln \frac{N}{N_0} = \frac{q}{v} \int_{T_{eq}}^T J(T) dT \quad (2.17)$$

Where v is the rate of cooling, and T_{eq} is the equilibrium temperature at the pressure of the experiment.

2.2. INDUCTION TIME OF GAS HYDRATE FORMATION

The interregnum sandwiched between the instant when the system converts metastable and the moment when the beginning of hydrate formation is spotted in the system with respect to hydrate formation is the induction time of hydrate formation (Kashchiev and Firoozabadi, 2003).

This time span is not deterministic and takes its distribution function, which is distinctive by the kind of nucleation, hydrate nuclei growth rate, the delicacy of detection devices, and so on. Then, the induction time stays not a severe and unambiguous system characteristic; it can fluctuate from several seconds to hundreds of minutes (Canale et al., 2019). However, an intensification in the driving force of nucleation frequently shrinkages the strew of induction time values detected in tests (Talaghat and Jokar, 2018).

Kashchiev and Firoozabadi (2003) derived a hypothetical formula for the most likely (average) induction time of hydrate formation (t_i) in experiments. They assumed that t_i corresponds to the instant when the degree of alteration of reactants to the hydrate is one percent, and it becomes conceivable to detect the hydrate phase in the system. They also contemplated two different types of nucleation:

- (i) The creation of new nuclei puissant of spontaneous growth and the growing of hydrate particles that take seemed earlier antecede in parallel (progressive nucleation)
- (ii) All nuclei stay shaped in the system in a rapid period of time, and then, merely the growth of the hydrate particles be accomplished (prompt nucleation).

The mathematical description of the growth of nuclei assumes that the growth rate does independently on the particle size and but it is an exponent of time.

In the class of isothermal hydrate formation conditions:

- for instantaneous nucleation,

$$t_i = \frac{K}{S-1} \quad (2.18)$$

- for progressive nucleation,

$$t_i = \frac{K}{\left(S(S-1)^{3m}\right)^{1/1+3m}} \exp\left(\frac{B}{(1+3m)\ln^2 S}\right) \quad (2.19)$$

In which S is computed the same as Equation (2.11).

In the case of isobaric conditions,

- for instantaneous nucleation,

$$t_i = \frac{K}{\exp\left(\frac{\Delta S_e \Delta T}{k_B T}\right) - 1} \quad (2.20)$$

- for progressive nucleation,

$$t_i = \frac{K \exp\left(-\frac{\Delta S_e \Delta T}{k_B T}\right)}{\left(1 - \exp\left(-\frac{\Delta S_e \Delta T}{k_B T}\right)\right)^{3m/1+3m}} \exp\left(\frac{B'}{(1+3m)T\Delta T^2}\right) \quad (2.21)$$

In Equations (2.18) to (2.21), K , B , and B' are constants, while m is the exponent in the power-law recitation the growth of the hydrate particles (varies from 0.5 to 1).

Jensen et al. (2008) found a decent correlation among the values determined by this technique and detected in the experimental formation of propane hydrate. Sarshar et al. (2008) applied a similar method to compute the induction times of hydrate formation for a hydrocarbon mixture. Wu et al. (2013) examined the necessity of the induction time of the formation of a binary mixture of propane and methane hydrate on the temperature and pressure.

For gas mixtures (Shin et al., 2012; Ohno et al., 2012) analyzed at supercooling of 6K and the pressure of 4300 kPa, the hydrate formation for 12000 seconds was only observed in sixty percent of experiments. In contrast, at the same pressure and 11K of supercooling, hydrates were shaped within less than ten minutes in all tests. There is a possibility of a hydrate to be nucleated first while it is under the metastable experimental conditions. The minor variations in the pressure of the system during this time (± 50 kPa) would have a tiny result on the system saturation (Skovborg et al. 1993). Figure 2.5 shows the computed required pressure and temperature of the induction

times for progressive nucleation of the methane hydrate for cases of homogeneous and heterogeneous nucleation.

Figure 2.5 - Induction times of methane hydrate formation at various (a) pressures ($T=273.2$ K, Equation (2.19)) and (b) temperatures ($P=19.4$ MPa, Equation (2.21)).

2.3. GROWTH OF GAS HYDRATES

Later gas hydrate nucleation, contents of the reactor consist of hydrate particles, liquid water (or ice), and the guest gas hydrate. Growth of the hydrate particles being determined by hydrate formation driving force. Driving force may define as an energy state. However, as determination of this state is not measurable, the difference from equilibrium state by means of thermodynamics, fluid flow, heat transfer, intrinsic kinetic rate, molecular diffusion, or even surface phenomena taking place in the system. Among different approaches, the models based on heat and mass transfer depend on the geometry of the system, the intensity of stirring (if exist), the heat extraction rate, and architecture of growth of hydrate iotas.

To create a mathematical model relating the hydrate formed amount as a function of time (kinetics of hydrate growth) and identify the rate-limiting are necessary. Such models are most needed and are applied, for instance, in the engineering for the planning of reactors for the hydrate's formation. So, the rate constants for proper hydrate formation reactions, which is, the essence of the inherent kinetics of the process, are regularly unidentified parameters in the hydrate formation kinetic models.

2.3.1 Models based on the chemical reaction

Vysniauskas and Bishnoi (1983) assumed a process with two steps, which started with the creation of a crystallization nucleus at the interface of the gas-water proceed by the succeeding growth of hydrate crystal everywhere of the formed nucleus, considering a reaction mechanism with three steps which were anticipated in their modeling as a semi-analytical model. In these three steps equations of rate, a preliminary gathering course was defined as

Representing the critical cluster formation was formulated by

And the hydrate crystal growing everywhere a stable nucleus was expressed by

By merging the planned mechanisms, the hydrate formation rate expressed as a function of the methane gas critical cluster concentrations at the boundary, and the entire surface area of the methane/ethane-water interface, which was stated as

$$r = k_r a_s [H_2O]^m [H_2O]_c^n [M]^q \quad (2.25)$$

In which the Arrhenius-type expression reaction rate constant is denoted by k_r , the overall surface area of the water-gas boundary is meant by a_s , while m , n , and q stand for parameters representative the reaction order with respect to each compound, and the critical size cluster represented by subscript c . Results of their experimental work exposed that the kinetics of formation were reliant on a_s , P , T , and the degree of sub-cooling (ΔT). Therefore, based on these critical quantifiable parameters a growth rate equation was planned as written in Equation (2.26)

$$r = A a_s \exp\left(-\frac{\Delta E_a}{RT}\right) \exp\left(-\frac{a}{\Delta T^b}\right) P^\gamma \quad (2.26)$$

In this formula, r characterizes the feeding rate of methane/ethane all through hydrate formation, and A is lumped pre-exponential parameter, a_s stand for the actual surface area of the methane/ethane-water boundary, ΔE_a is apparent energy of activation for hydrate formation, R is the universal gas constant, T is absolute temperature, a and b are empirical parameters, P is absolute pressure and γ is the overall order of the reaction. In the above equation, ΔT represents the degree of supercooling, which is equal to the difference between the experimental temperature and the hydrate-liquid and water-gas equilibrium temperature corresponding to the experimental pressure. Table 2.1 sum up the kinetic rate parameters for methane and ethane hydrate fitted in their semi-analytical model founded on the formulation of the chemical reaction.

Table 2.1 - Results of the kinetic parameter fitting for methane and ethane formation of hydrate in the semi-analytical chemical reaction of Equation (2.26).

Guest gas	Kinetic rate parameters				
	A (cm.min ⁻¹ .bar ⁻¹ .y ⁻¹)	ΔE_a (kJ.mol ⁻¹)	γ	a	b
CH ₄	2.400×10 ⁻²⁹	-106.204	2.986	0.0778	2.411
C ₂ H ₆	4.552×10 ⁻²⁶	-133.015	2.804	0.0778	2.411

Source: (Vysniauskas and Bishnoi, 1985)

Table 2.1 compares parameters for methane and ethane hydrates and shows the scale of the interaction between guest gases and water, which its activation energy implies the formation of ethane hydrates that need a greater quantity of the activation energy.

Different researchers extended the semi-analytical equation developed by Vysniauskas and Bishnoi (1983).

Topham (1984a) fixed this equation to the system of growing natural gas hydrates in seawater rising gas bubbles of hydrocarbon. Considering the mass balance equation and natural gas bubble transport properties and the quantity of rising bubbles, the model was upgraded, including bubble lifetime and radius of bubble against the depth of water. The obtained information from hydrate growth in a single rising bubble stood further assumed to develop a complete model of bubble plume, and the results were used to assess a theoretical situation of an oil-well blowout (Topham, 1984b).

Elperin and Fominykh (1995) studied c gas hydrate growth at the surface of a gas slug in a water-filled channel. They investigated gas hydrate formation at the surface of a gas slug fixed in a channel by a descendant fluid flow and gas hydrate formation at the surface of a gas slug rising in a water-filled channel.

Lekvam and Ruoff (1993), through using a reaction kinetic approach, modeled methane hydrate formation in liquid water. Based on their experimental evaluations, they planned a reaction model involving five pseudo-elementary courses which showing the hydrate formation in three go-ahead stages of:

- (i) gas is dissolving into the water
- (ii) gas building-up of hydrate nuclei
- (iii) through a spontaneous process, methane hydrate growth is keeping on.

The rate equations involved nine constants in total; however, the developed model consists of five equations. Two of the nine rate coefficients stood tangled in initial methane gas dissolution and were obtained from experimental measurements. The other seven rate coefficients were gained by fitting the experimental data. A good agreement among model returned output and experimental data was found in their job with the induction time well estimated. Certain the high number of fitting coefficients, the good agreement with the experiments is anticipated. However, the predictive competences of the method cannot be deduced from the work.

Assuming instant hydrate nucleation in a specific sub-cooling ($\Delta T = 6.5$ K), the hydrate growth can be computed by two adjustable constants (Boxall et al., 2009):

$$r = uk_1 \exp\left(\frac{k_2}{T}\right) As(T_{eq} - T_{sys}) \quad (2.27)$$

This kinetic rate coefficient was fitted to experimental data and implemented in the commercial flow assurance software of Schlumberger OLGA (2016).

2.3.2 Models based on mass transfer

From transport phenomenology next to gas hydrate nucleation, the system contains liquid water (or ice depending on the system temperature), hydrate particles and, the hydrate guest gas. Such hydrate particle growth in the system is taking place by the hydrate formation kinetic characteristics and determined through mass and heat transfer processes. These determining parameters rely on the geometry of the system (reactor), the attendance of stirring (and its magnitude), the heat extraction rate, and the growth morphology of particles of the formed hydrate.

The rate constants for appropriate reactions of hydrate formation, that is, features of the inherent kinetics of the process, are usually unidentified parameters in the hydrate formation kinetic equations. In the engineering design strategy of reactors for the formation of hydrate, these parameters are most demanded and are used (Heidaryan et al., 2010).

Englezos and colleagues (1987) offered a model for intrinsic kinetic just with one fitting parameter for the methane and ethane gas hydrates formation. In their model, the driving force was characterized as a difference between the fugacity of the dissolved methane/ethane and the hydrate three-phase experimental temperature equilibrium. Figure 2.6 shows the concept of the kinetic model was expressed stand on the theory of crystallization growth for the particle of hydrate coupled with the theory of two-film at the gas-liquid interface that explaining the phenomena of mass transfer.

Figure 2.6 - Concept of the Englezos and coworkers hydrate growth model (a) Concentration profile at the gas-liquid interface (two-film theory) (b) Graphic of the semi-batch reactor where hydrate slurry forms (c) Fugacity profile in the diffusion-adsorption layer around a growing hydrate particle.

Source: (Yin et al., 2018)

This model in mathematical form represent as

$$\frac{dn}{dt} = K^* A_p (f - f_{eq}) \quad (2.28)$$

In this model, mass transfer is the controlling mechanism, and the fugacity difference of gas-phase acts as the driving force. The A_p in this formula is hydrate particle surface area, and f is fugacity of guest gas, and the subscript of eq refers to equilibrium. Just with one adaptable parameter K^* which is the overall kinetic rate constant

$$\frac{1}{K^*} = \frac{1}{k_r} + \frac{1}{k_d} \quad (2.29)$$

It includes both effects of mass transfer rate k_d and rate of absorption “reaction” k_r .

By integrating the rate per particle for all particles of any size, it may be formulated a global reaction rate for all the particles as:

$$\frac{dn}{dt} = \int_0^\infty (dn/dt) \phi(r, t) dr = 4\pi K^* \mu_2 (f - f_{eq}) \quad (2.30)$$

and

$$\mu_2 = \int_0^\infty r^2 \phi(r, t) dr \quad (2.31)$$

Where ϕ is the distribution of hydrate particle size, and μ_2 is the second moment of the particle size distribution. Smaller particle size leads to a higher number of particles in a given volume (see Figure 2.7).

Figure 2.7 - Different sphere size leads to different total sphere surface for a constant particle fraction

Source: (Folk; Ward, 1957)

The particle surface area can be several orders of magnitude higher for smaller particles, and it is controlling by summation of the surface of all particles, which is $\mu_2(t)$.

In this view, when the gas phase is transported into contact with the liquid phase, to describe the phenomena, the two-film theory (Figure 2.6a) was applied. The rate of gas diffusion from the interface of the gas-liquid to the liquid film was considered to be the same with the gas consumption rate from the liquid film to the bulk solution, so the condition of quasi-steady-state was presumed with no term of accumulation in the liquid film. In a shell of the liquid film with a thickness of δ the mass balance of the gas molecule can be stated (Froment et al., 2011)

$$D \frac{d^2 C}{dy^2} = 4\pi K^* \mu_2(t)(f - f_{eq}) \quad (2.32)$$

Assuming the number of moles of the water remains almost constant, and the liquid solution can be assumed as ideal, so the concentration of gas in the aqueous phase at three-phase equilibrium can be calculated by relating fugacity to gas concentration through using Henry's law, so boundary conditions of Equation 2.32 are:

$$\begin{aligned} C(0) &= C_{eq} & Y(0) &= f_g - f_{eq} \\ & & \text{or} & \\ C(\delta) &= C_b & Y(L) &= f_b - f_{eq} \end{aligned} \quad (2.33)$$

Analytical solution of this ordinary differential equation (ODE) with the above boundary conditions yields the fugacity profile for the gas in the liquid film

$$f(y) = f_{eq} + \left(\frac{1}{\sinh(\gamma)} \right) \left((f_g - f_{eq}) \sinh \left(\gamma \left(1 - \frac{y}{\delta} \right) \right) + (f_b - f_{eq}) \sinh \left(\gamma \frac{y}{\delta} \right) \right) \quad (2.34)$$

where γ is the Hatta number given by:

$$\gamma = \delta \sqrt{\frac{4\pi K^* \mu_2}{D^*}} \quad \& \quad D^* = \frac{D_{C_{w,0}}}{H} = D \left(\frac{C_{eq} + C_{w,0}}{H - f_{eq}} \right) \quad (2.35)$$

That shows how fast the reaction goes forward in comparison with rate of the diffusion through the hydrate shell. As well as H stands for constant of Henry's law; D is the guest gas diffusion coefficient in the aqueous phase and, $C_{w,0}$ is the initial concentration of water; f_g is the fugacity of pure gas at the experimental temperature and pressure, and f_b is the fugacity of gas in the bulk of water.

Furthermore, the flux of gas being transported to the aqueous phase at the boundary can be resulting from at the interface of gas-liquid surface area A_{g-l} :

$$\frac{dn}{dt} = J_{y=0} A_{g-l} = \frac{D^* \gamma A_{g-l}}{\delta} \frac{(f_g - f_{eq}) \cosh(\gamma) (f_b - f_{eq})}{\sinh(\gamma)} \quad (2.36)$$

The initial condition for this equation is the moles of the gas number that have been transported into the aqueous phase from beginning until the “turbidity point.” It can be obtained from the experimental data. It has been presumed in the model that at the turbidity point, the fugacity of gas in the bulk of aqueous phase drops to the three-phase equilibrium value promptly.

To guesstimate $\mu_2(t)$, the model of the population balance could be assumed with the rate of linear growth, which is independent of the secondary nucleation rate (relative to the second moment of the particle size distribution) and the crystal size. Hence, the general population balance can be applied

$$\frac{\partial \phi}{\partial t} + \frac{\partial (G\phi)}{\partial r} = \theta \phi(r) \quad (2.37)$$

Which may be simplified to

$$\begin{aligned} \frac{d\mu_0}{dt} &= \alpha_2 \mu_2 & \mu_0(0) &= \mu_0^0 \\ \frac{d\mu_1}{dt} &= G\mu_0 & \mu_1(0) &= \mu_1^0 = 2r_c \mu_0^0 \\ \frac{d\mu_2}{dt} &= 2G\mu_1 & \mu_2(0) &= \mu_2^0 = 4r_c^2 \mu_0^0 \end{aligned} \quad (2.38)$$

Simultaneously solving these equations will result in obtaining $\mu_2(t)$. However, to stay a model just with one fitted coefficient, the constant of nucleation rate (α_2) was set to be 10^{-3} , which connoted that there was no secondary nucleation because of crystal breakage. Englezos et al. (1987) also argued that predictions of the model were not sentient to the values of α_2 up to 10^{12} .

Another constraint is the hydrate nucleus critical size, which was computed through using the theory of homogeneous nucleation that considered the Gibbs free energy of the system regarding the creation of a film and a new phase formation as

$$r_c = \frac{2\sigma}{\left(\frac{RT}{V_H}\right) \left(\ln \left(\frac{f_b}{f_{eq}} \right) + \frac{vV_w (P_{exp} - P_{eq})}{RT} \right)} \quad (2.39)$$

In which σ stands for the surface tension of hydrate-water, V_H and V_W are the molar volumes of hydrate and water, respectively. The parameter of v is the hydration number.

The initial particles number of μ_0^0 was calculated from a mass balance equation for the gas used up at the point of turbidity

$$\mu_0^0 = \frac{3M_H(n_{tb} - n_{eq})}{4\pi V_L \rho_H r_c^3} \quad (2.40)$$

In which the molecular weight and the density of hydrate are represented by M_H and ρ_H , the parameter of n_{tb} stands for the amount of dissolved gas, and n_{eq} is the amount of gas that can be dissolved at a pressure corresponding to the three-phase equilibrium.

Considering all the above governing equations, a mean of the hydrate growth rate can be expressed as follows just with one fitting parameter (K^*) as

$$G_{avg} = \left(\frac{K^* M_H}{\rho_L} \right) \left(y_L \frac{(f_g + f_b - 2f_{eq})(\cosh(\gamma) - 1)}{\gamma \sinh(\gamma)} + (L - \delta)(f_b - f_{eq}) \right) \quad (2.41)$$

The parameters K^* , which is the combined rates was calculated by means of the least-square method under different temperatures, where the speed of stirring was 400 rpm due to remove the resistance of the mass transfer about the hydrate particles.

As is evident in Table 2.2, fitted values of K^* have a fragile dependence on temperature. And as argued, no chemical reaction has involved during hydrate formation (Englezos et al. 1987).

Table 2.2 - Kinetic rate parameters for methane hydrate growth in fugacity based model

T/K	274	276	279	282
$K \times 10^5 / \text{mol.m}^{-2}.\text{s}^{-1}.\text{MPa}^{-1}$	0.65	0.55	0.57	0.58

Source: (Englezos et al. (1987)

Skovborg and Rasmussen (1994) pointed out two crucial coefficients of the initial amount of gas dissolved in the water, and the intrinsic rate constant is the main limitation of the model proposed by Englezos et al. (1987). They suggested a shortened model created on the postulation that the conveyance of gas molecules from the gas phase to water remained the rate-determining stage in the entire formation process of the hydrate. Consequently, the model of particle population balance can be

detached, and accordingly, a little relation among the amount of consumed gas and the total surface area of hydrate particles can be applied. Accordingly, the rate of used mass can be defined by

$$\frac{dn}{dt} = k_L A_{g-l} C_{w,0} (x_{int} - x_b) \quad (2.42)$$

In which the mole fraction of gas in the aqueous (at the interface of water-gas in equilibrium point) denoted by x_{int} and, x_b is the mole fraction of gas in the bulk water phase in equilibrium with the hydrate phase at operating temperature and pressure. As well as k_L is the calculated mass transfer coefficient. However, to be applied, this model needs a chronological evolution of mole fractions of the gas at the interface and in the liquid bulk. As the stage of rate-limiting mass transfer at boundary presumed only practical to a stirred tank reactor with considerable resistance in mass transfer at the interface, this model was not widely used. Malegoankar et al. (1997) corrected a minor inconsistency in the model; in the population balance of the model, particle diameter was using than they changed it to the radius. Further inspection of the population balance model carried out by Herri et al. (1999) which used the prior kinetic models in a stirred tank reactor and assumed the rate-limiting step as the mass transfer in the liquid-gas interface rather than at the hydrated particle crystallization region proposed by Skovborg and Rasmussen (1994). So, mass conservation for methane soluble in bulk is accepted, counting two terms describing the hydrate growth rate and mass transfer rate. Population balance equations (PBE), which took both primary nucleation “birth rate”, and secondary nucleation, breakage, and agglomeration “death rate” due to agglomeration has been used. Each part in the PBE was analyzed and articulated clearly based on advanced crystallization theory and mass transfer. Finally, a set of eight partial differential equations (PDE) were derived and solved numerically, and a sufficient simplified model of primary nucleation/growth was shown.

Their shortened primary nucleation/growth model was applied enough to clarify the effect of the rate of stirring on initial hydrate diameter and particle number. But secondary nucleation instigated by abrasion was recognized to be controlling just at a high, stirring speed, although agglomeration did not offer a virtuous clarification on the rise in the mean diameter of hydrate particles.

Clarke and Bishnoi (2005) upgraded the kinetic model by introducing an in-situ particle size analysis into the system during hydrate formation. The second moment of hydrate

particle size distribution was determined experimentally by instrumentation, rather than by calculation through the population balance model. They used data from a focused beam reflectance method (FBRM) probe with an infrared laser, with a wavelength of 785 nm, is housed in a cylindrical probe, and rotates at a high velocity, which could measure chord lengths 0.5-1000 μm for in situ particle size analysis. It removed the necessity to solve the system of three coupled ODEs for the $\mu_2(t)$.

2.3.3 Models based on the combination of mass transfer and chemical reaction

Hashemi et al. (2007) reformulated the model of Englezos et al. (1987) based on a driving force of gas concentration with the formation kinetics of hydrate. They expressed the rate of reaction as

$$R(t) = \pi\mu_2(t)K^*(C - C_{eq}) \quad (2.43)$$

$$\frac{1}{K^*} = \frac{1}{k_r} + \frac{1}{k_s} \quad (2.44)$$

Where obtained from population balance, the parameter of $\mu_2(t)$ is the second moment of particle size distribution. As well as the overall kinetic rate constant is related to the rate constant of intrinsic kinetic (k_r) and the coefficient of mass transfer for the diffusion of the gas in aqueous (from the solution bulk) to the hydrate-liquid interface (k_s). Hashemi et al. (2007) provided an ephemeral examination of the temperature difference crosswise the film of liquid at the vapor-liquid interface and showed that ΔT inside the hydrate film is minimal. Therefore, the driving force for hydrate growth can be based on the two-phase (water-hydrate) equilibrium instead of the three-phase equilibrium condition (Gas-Liquid-Hydrate). In their work, they used transport parameters from the model of Malegoankar et al. (1997) and gas consumption rate data reported by Clarke et al. (2007). Bergeron and Servio (2008) examined the kinetic rate of hydrate formation in a closed-loop system by using a particle size analyzer with the minimum quantifiable particle diameter down to 0.6 nm. The overall resistance to hydrate growth is represented by:

$$R = \frac{1}{A_p} \left(\frac{1}{k_{H-L}} + \frac{1}{k_r} \right) + \frac{1}{K_{L-V}} \quad (2.45)$$

Where A_p is the total solid surface area (hydrate particles), k_{H-L} the mass transfer coefficient in the diffusion layer around the hydrate particle, k_r the reaction rate constant, and $1/K_{L-V}$ is the V–L_w interfacial resistance. By comparing the ratio of the convective mass transfer to the rate of diffusive mass transport (Sherwood number: Frossling, 1938:) of the gas side and the liquid side of the V–L_w interface it can be assumed that the resistance on gas side is negligible for solid particles in an agitated vessel (Tatterson, 1991) so it can be written as

$$Sh = \frac{k_{H-L}}{D_{g-w}} = 2 + 0.6\sqrt{Re}\sqrt[3]{Sc} \quad (2.46)$$

Where D_{g-w} is the diffusivity of the gas hydrate former in water, Re the Reynolds number, and Sc is the Schmidt number. Bergeron and Servio (2008) assumed a stationary film with a diameter of 6 μm in the right-hand side of Equation (2.46) and substituted the result of the diffusion coefficient of Wilke and Chang (1955) in left side estimated order of k_{H-L} about 10^{-5} m.s^{-1} . As reported by Clarke and Bishnoi (2005) order of k_r in hydrates with sl formation is 10^{-8} m.s^{-1} , so considering that $1/k_{H-L}$ is negligible compared to $1/k_r$ is a logical assumption. Bergeron and Servio (2008) used this simplification of Equation (2.45) in combination with driving force proposed by Hashemi et al. (2007) wrote the number of moles consumed for hydrate growth as

$$\frac{dn}{dt} = \frac{C_{w,0}(x_{L-V} - x_{H-L})}{\frac{1}{A_p k_r} + \frac{1}{K_{L-V} A_{L-V}}} \quad (2.47)$$

Where $C_{w,0}$ is the initial concentration of water in the bulk liquid phase (assumed to be constant), x_{L-V} is the gas hydrate former solubility in the liquid phase at the V–L_w interface (at V–L_w equilibrium) and x_{H-L} is the gas hydrate former solubility in the liquid phase at the H–L_w interface (at H–L_w equilibrium). The interfacial area at the vapor-liquid water interface is denoted by A_{L-V} .

It may be possible to assume spherical particles, then the total solid surface area as a function of the second moment of the particle size distribution so

$$\frac{dn}{dt} = \frac{C_{w,0}(x_{L-V} - x_{H-L})}{\frac{1}{\pi\mu_2(t)V_L k_r} + \frac{1}{K_{L-V} A_{L-V}}} \quad (2.48)$$

Where V_L is the volume of liquid in the crystallizer. Equation (2.48) may rearrange for the reaction rate constant as

$$\frac{dn}{dt} = \frac{V_L \rho_W}{MW_W} \frac{(x_{L-V} - x_{H-L})}{\frac{1}{\pi \mu_2(t) V_L k_r} + \frac{1}{k_{L-V} a_{L-V}}} \quad (2.49)$$

Where ρ_W is the density of water, MW_W the molecular weight of water, and $k_{L-V} a_{L-V}$ is the dissolution rate in the liquid film at the V–L_W interface.

Bergeron et al., (2010) assumed it is possible to experimentally determine the mole fraction of the gas hydrate formed in the bulk aqueous phase during hydrate growth. So, by eliminating the confrontation at the interface of water-vapor it can be carried out. This type of tactic links to the standard engineering style where the rate is identical to the proportion of the driving force to the resistance. As far as, the driving force to growth of hydrate is no more comprise the interface of water-vapor, the conforming resistance is individually containing the one due to kinetics of hydrate. Combining the mole fraction of the gas hydrate formed in the bulk of aqueous phase, Equation (2.49) became:

$$\frac{dn}{dt} = \frac{V_L \rho_W}{MW_W} \frac{(x_L - x_{H-L})}{\frac{1}{\pi \mu_2(t) k_r}} \quad (2.50)$$

Where x_L is the mole fraction of the guest gas in the bulk of aqueous phase at the experimental conditions (two-phase), as well as x_{H-L} is the solubility of the guest gas under hydrate-liquid water equilibrium (three-phase) at the temperature and pressure of experiment.

2.3.4 Models based on heat transfer

As discussed by Freer et al. (2001), a model for growth kinetic could be planned with sub-cooling (ΔT) as a driving force defined. They assumed the effect of heat transfer is dominating in the crystallization and growth phenomena, and mass transfer was negligible, so continuous growth mechanism with high interfacial driving force (Tiller, 1991) considered. In such a hydrate formation, the kinetic model could be considering, both the intrinsic kinetics and heat transfer effects. In conclusion, regression to experimental data has been used to determine three unknown parameters, which consist of two kinetic rate parameters and one heat transfer coefficient. In this way, the kinetics of molecular attachment were presumed to follow the Arrhenius type function, and the heat transfer coefficient was set to be constant. By applying a high-pressure

reactor equipped with optical microscopy technique through visualization window Freer et al. (2001) measured the rate of methane hydrate film growth at the water-methane interface in the temperature range of 274.2–277.2 K and pressure range of 3.55–9.06 MPa. Based on the 1D energy conservation assumption, a moving boundary model was established. So, the hydrate interface was mimicked as a moving boundary parallel to the interface in the water phase.

The model developed based on below key assumptions:

- (a) The temperature at the moving boundary is equal to the equilibrium temperature
- (b) The temperature difference of (ΔT) within the hydrate phase is insignificant
- (c) Water is thoroughly wetting the hydrate film.

Figure (2.8) shows a graphic of the hydrate film growth at the methane-water interface (Mochizuki; Mori, 2006).

Figure 2.8 - Schematic of hydrate film growth kinetic models based on heat transfer (1D energy conservation equation)

Source: (Mochizuki; Mori, 2006)

Considering the above assumptions, its governing equation of can be articulated as

$$\frac{\partial T}{\partial t} + V_x \frac{\partial T}{\partial x} = \alpha_w \frac{\partial^2 T}{\partial x^2} \quad (2.51)$$

And the initial condition and associated boundary conditions are

$$\begin{aligned} I.C.: \quad T(0, x) &= T_{bulk} \\ B.C.1: \quad T(x, X(t)) &= T_{eq} \\ B.C.2: \quad -k_w \frac{\partial T(x, X(t))}{\partial x} &= \rho_H \lambda_H \frac{dX}{dt} \end{aligned} \quad (2.52)$$

Where the bulk water phase temperature is denoted by T_{bulk} , the velocity of the fluid in the x-direction is designated by V_x , the thermal diffusivity of water is written as α_w , ρ_w is the water density, λ_H stand for the hydrate dissociation heat, dX/dt is the moving

interface velocity, and k_w represents the thermal conductivity of water. Freer et al. (2001) analytically solved this PDE for the velocity of the moving boundary and evaluated it with the experimental rate of hydrate growth. They concluded due to thermo-capillary convection (through convection the extra heat transfer occurred), a significant disparity between the two results has occurred. So, a model by combining both interfacial growth kinetics effect and convective heat transfer effect was projected to characterize the rate of growth as

$$\lambda_H \rho_H \frac{dX}{dt} = K(T_{eq} - T_{bulk})$$

$$\frac{1}{K} = \frac{1}{k} + \frac{1}{h} \quad (2.53)$$

Where K stands for the total resistance, the heat transfer coefficient denotes by h , and k is the guest gas coefficient of kinetic rate. Regarding the results of thin wire test for heat transfer, it is fair enough to accept a constant heat transfer coefficient.

The coefficient of kinetic rate is planned to be expressed by an Arrhenius-type function

$$k = k_0 \exp\left(-\frac{E_a}{RT_{eq}}\right) \quad (2.54)$$

Where k_0 is the pre-exponential factor, and the activation energy denoted by E_a . The final equation has three unknown parameters which need to be regressed from the data using a least-squares method. Values for the regressed parameters are given in Table 2.3 for the guest gas of methane.

Table 2.3 - List of kinetic coefficients calculated in the heat transfer model

Parameter	k_0 (W.m ⁻² .K ⁻¹)	E_a (kJ.mol ⁻¹)	h (W.m ⁻² .K ⁻¹)
	1.60567×10^{36}	171	42326

Source: (Freer et al. 2001)

The heat transfer coefficient had good agreement with calculated values through the thin wire for Reynolds number ranging from 10^{-5} to 10^{-2} and film thickness of 2 to 5 μm . The range of thickness of film was in the scale value reported by Makogon et al. (1998) for films of methane hydrate (5 μm). However, the energy of activation was found to be greater than values reported by (Mullin, 2001) for surface integration (40–60 kJ.mol⁻¹), and diffusion (10–20 kJ.mol⁻¹). Furthermore, the appraised heat transfer coefficient as a result of convection very well conceded with the computed values which reported through the thin-wire approximation model (Kurdyumov and Fernandez, 1998).

Mori (2001) planned a humble model of convective heat-transfer in which the cross-growth rate of hydrate shell was relative to $\Delta T^{1.5}$ with respect to the effective temperature driving force. Its graphic is illustrated in Figure (2.9).

Mochizuki and Mori (2006) accepted a significant effect of the conductive heat-transfer theory. They assumed the shell front to the surroundings as the stage of rate-controlling, which was formerly unkempt by Freer et al. (2001). A kinetic model was then established by using a model of transient conductive heat-transfer for two hydrate film geometries of two-dimension, one with a conventional hydrate film front and the other with a semi-circular hydrate film front as publicized in Figure 2.10.

Figure 2.9 - Diagram of film growth of hydrate kinetic models based on model of convective heat-transfer

Source: (Mochizuki; Mori, 2006)

Figure 2.10 - Schematic of hydrate film growth kinetic models based on 2D convective heat-transfer model

Source: (Mochizuki; Mori, 2006)

For methane hydrate at $P = 9060$ kPa by numerical solving the governing PDEs film, thickness was estimated to be $10\text{--}20\text{ }\mu\text{m}$. However, in this study, one contradictory outcome was attained, which was that hydrate films exhibited a propensity to be thin with an intensification in the sub-cooling (ΔT) of the system.

By assuming that the hydrate film thickness is proportional to the inverse of the driving force, (ΔT), Peng et al. (2007) enhanced the convective heat transfer model of Mori (2001).

The lateral hydrate film growth rate was thus derived from being proportional to the power of 2.5 with respect to the temperature driving force, by revealing a single gas bubble to water, the early hydrate shell thickness and its growth under different sub-cooling conditions measured by Li et al. (2014). The concluded the thickness of the hydrate film remains on the order of $10\text{ }\mu\text{m}$ as well as the lateral growth rate of hydrate shells very well can be explained with $\Delta T^{5/2}$. Table 2.4 listed the calculated parameter (ψ), which is a result of fitting in the relation between the sub-cooling (ΔT) to the power of 2.5 and hydrate film growth rate (r).

Table 2.4 - Values of ψ in the heat transfer model of the growth rate of hydrate film $r_H = \psi \Delta T^{5/2}$

T/K	273.4	275.4	277.4	279.4
Hydrate growth rate parameter (ψ)	2.76	3.31	3.86	4.46

Source: (Li et al. 2014)

Meindinyo et al. (2015) proposed another simple heat balance model to analyze methane hydrate growth under constant pressure in a stirred-tank reactor. Combining hydrate formation heat, the reactor wall heat transfer rate, and the heat buildup rate inside the reactor, the model developed based on the energy conservation equation. As they discussed that the heat transfer coefficient varied along the hydrate formation process, so the heat transfer coefficients need to be fitted over the experimental temperature measurement. In conclusion, they found an acceptable result between the gas consumption predicted by the model and measured experimental data. It should be noted that such a semi-empirical kinetic model has limitations are:

- (a) it is restricted to the experimental setup laboring in that particular work
- (b) expressively this model relay on the fitted parameters.

It is considerable to note that these certain models of kinetic considering the essential mechanism of heat transfer of hydrate growth and assessing the rate of hydrate growth mainly focus on the boundary of water and phases of hydrate former.

In conclusion, the disparity of different heat-transfer conquered kinetic models planned is mainly because of the different reactor shape, the location of the hydrate shell comparative to the interface, and the controlling process of heat transfer (either convection or conduction).

In these models, the driving forces defined as the difference in temperature between the equilibrium temperature and the hydrate film. This is different from the standard driving force, which defined as the difference in fugacity or concentration, which is classically applied in models of mass-transfer based.

Admittedly the role of heat transfer is weighty throughout the course of hydrate growth because of its natural robust exothermic reaction, which linked to great enthalpy change (Sloan; Fleyfel, 1992). Nevertheless, it is also obvious that the outcomes gotten from these class of kinetic models have restrictions, which stalwartly hinge on the assumed initial conditions and boundary conditions. These circumstances remain tough to confirm with the present experimental methods (because of its tiny scales and extreme scale of time) and maybe impractical occasionally. Besides, it was also declared that the internal edifice of the hydrate shell was not vibrant up to now (Sun et al., 2010), which possibly will consequence in a natural transient of thermal properties, coefficients of heat transfer (Meindinyo et al., 2015) and perimeter the appropriateness of these planned approaches.

2.4. DIFFERENT APPARATUS FOR STUDYING KINETICS OF GAS HYDRATES

The principal method in hydrate kinetic is the quantify of the amount of the gas used upon hydrate formation or got out upon hydrate decomposition at measured temperature and pressure. Still, a broad range of other modern physicochemical apparatus has been used in the examination of the formation and decomposition of gas hydrates. Extra information by other methods, in summary, are gathered below.

2.4.1 Optical microscopy

The method of optical microscopy served to study the macroscopic and morphology specifications of the hydrate particles growth and the kinetic of fabrication of the hydrate shell at the interface of water-gas (Melnikov et al., 2010; Kitamura; Mori, 2013). It is a direct method for monitoring processes on a real time scale. Principally, tests of this type are doing by applying a high-pressure cell equipped with two visual hatches situated contrary to each other, which permits inspection in a 'transmission' geometry. The procedure of contemporary automatic instrumentation for examine the nucleation of hydrates at the interface of water-gas stands on the ocular recording of the hydrate formation moment.

Gas hydrates are inherently transparent and frequently form delicate crystals, whose refractive index is moreover very close to that of water. Consequently, imaging of bright field, found on absorption, refraction, or reflection of light, generally provides images with poor resolution. For example, in an aqueous medium, edges of hydrate crystal can be hard to detect. Contrast methods working using assumption other than light adsorption or refraction are, then, predominantly well-suited to gas hydrates. Some subcategories of optical microscopy are Differential interference contrast (Min et al., 2020), Darkfield imaging (Delzeit; Blake, 2001), Fluorescence imaging (Bai et al., 2010), and Reflection microscopy (Touil et al., 2019).

2.4.2 Thermal and calorimetric methods

In this method, measurable data regarding the hydrate process is obtaining by means of the calorimetric technique through measuring the heat change due to hydrate formation or upon hydrate dissociation as a function of time or either temperature of the system. This method stands hinge on the law that hydrate dissociation is endothermic, while hydrate formation is an exothermic process. It is a comparatively humble technique based on the sample temperature measurement (Dalmazzone et al., 2009; Daraboina et al., 2011; Stoporev et al., 2019) which is extensively applied for the measurement and semiquantitative disclosure of the onset and endset of hydrate formation and dissociation process. As the changed heat is relative to the quantity of formed or decomposed hydrate and the enthalpy of equilibrium of majority of hydrates is known, the calorimetric technique may be served to assess the total quantity of hydrate that has dissociated in the system.

2.4.3 Diffraction methods

The powder X-ray and neutron diffraction can be used in kinetic measurements (Wang et al., 2002; Staykova et al., 2003; Kuhs et al., 2006). However, it needs a specimen prepared flawlessly because just in such a way intensity of the crystalline phase reflections in the patterns of powder X-ray diffraction is proportional to the amount of this phase change in the cell. This link stirs approaches to quantitative diffraction. It is notable that methods of diffraction make data available not only on the number of phases in the sample but also on the composition of the phases. Definitely, one of the main necessities for using diffraction methods is the attendance of crystallites with all possible spatial orientations. Additionally, all orientations have to be equally probable, so the requirement of 'perfect' specimen preparation executes substantial limitations on the application of diffraction methods for kinetic tests. As an X-rays low penetration aptitude, the volume of the specimen intricate in the diffraction is usually moderate (of the order of several cubic millimeters). This state may barely be satisfied in the powder diffraction experiments of hydrate kinetics.

2.4.4 Nuclear magnetic resonance spectroscopy

The signal position in the Nuclear Magnetic Resonance (NMR) spectrum is actually keen to the molecule environment covering the nucleus, which makes it likely to discriminate between molecules of guest gases positioned in different types of cavities (Pietrass et al., 1995; Kini et al., 2004). The intensity of the signal in the NMR spectrum is relative to the entire quantity of nuclei of a specific sort, so it offers data on the entire sample volume. Nevertheless, due to the high cost of the apparatus and to the difficulty of regulating the equipment to measure at high pressures, using NMR spectroscopy for investigations of kinetics of hydrate formation and dissociation are still scarce. The main value of the results by NMR is linked to mechanisms of nucleation and growth instead of the rate of hydrate formation.

2.4.5 Raman spectroscopy

As the typical vibrational of the guest molecules frequencies are varying depending on their environment, it is likely to consistently measure the frequencies for molecules located in small and large cavities of hydrates and molecules dissolved in the water

bulk. So, the Raman spectroscopy technique is widely used to study gas hydrates (Sum et al., 1997) as is conceivable to distinguish the occupancy ratio of large and small hydrate cavities and the fraction of molecules not merged in the hydrate (Subramanian; Sloan, 1999) from the Raman spectral bands intensity ratio. Nevertheless, this technique contributes data about a rather small volume, which cannot sufficiently characterize the whole sample (Murshed et al., 2010).

2.4.6 Nephelometry

Approaches based on light scattering, so the hydrate formation and growth processes also may be examined. Regarding nephelometry, which is a measurement of the intensity of light scattered at a particular angle, it is conceivable to basically evaluate gas hydrates (Parent; Bishnoi, 1994). The onset of hydrate formation in the solution was spotted by a rise in the intensity of the light scattering. Nephelometry may also be applied to spot the hydrate formation onset, to understand the rate of hydrate growth, and to acquisition composition of the hydrate (Sauter et al., 2006). But it does not offer data regarding the crystal's characteristics formed in solutions such as geometry and concentration. This method has been used for determination the induction times in ethane hydrate formation (Servio et al., 2000).

2.4.7 Static light scattering

Laser diffraction or static light scattering may be used for determining the concentrations and sizes of particles of hydrate accumulated in solution (Monfort and Nzihou, 1993). The technique is relays on the examination of the angular dependence of the laser radiation intensity scattered by the sample. This method may be used on a real-time basis to examine the kinetics of nucleation of the new phase. Though, this technique is not applied for micrometer-sized particles, only for particles of less than one micrometer in size. To compute the hydrate particle size, it is also essential to identify the refractive index of the hydrate crystal, which can be determined by other experimental or hypothetical methods (Herri and Gruy, 1995; Bylov; Rasmussen, 1997).

2.4.8 Multi-wavelength extinction

The concentration and size of hydrate particles may be measured through the technique of multi-wavelength extinction, which consists in determining the turbidity point from the reduction in the light intensity after it has been passed through the sample (Herri and Gruy, 1995; Herri et al., 1999b). A procedure has been developed for the determination of the concentration and size of hydrate particles in the solution by spotting of the turbidity at two different wavelengths (Herri et al., 1999a). This method was appropriate and acting as a decisive factor to determine the concentration and average size of particles of different gas hydrates on a real-time basis. However, refractive of the hydrate crystals ought to be known for the practice of this technique.

2.4.9 Focused beam reflectance

The focused beam reflectance technique has been applied to determine the sizes and concentrations of hydrate particles (Clarke and Bishnoi, 2005; Al-Otaibi et al. 2010; Giraldo, et al. 2013). By means of this technique, particle size distribution was measured, and the hydrate particles concentration in the aqueous phase was specified. Still, like other optical methods, the range of sizes available for measurements is limited by the limit of diffraction.

2.4.10 Dynamic light scattering

Dynamic light scattering has been applied to the determination of the nanoparticle size in colloidal systems (Yousif et al., 1994; Uchida et al. 2003). By means of this technique, it is conceivable to determine the particle size distribution and the particles average hydrodynamic diameter (Nerheim et al., 1994). Fortunately, using this method without knowing the refractive index, the particle size can be measured. In comparison with methods of laser diffraction and turbidimetry, it is superior. However, to the true measurement of the hydrodynamic particle size, it is essential to identify the refractive index and the viscosity of the medium (Uchida et al. 2003).

Nomenclature

A	attachment of building units to the nucleus
A	lumped pre-exponential parameter (Eq. 2.26)
A_{g-l}	interface of gas-liquid surface area
A_{L-V}	interfacial area at the vapor-liquid water interface
A_p	hydrate particle surface area
a_s	overall surface area of the water-gas boundary
B	constant
B'	constant
C	concentration
c	shape factor
D	guest gas diffusion coefficient
f	fugacity
f_b	fugacity of gas in the bulk of water
H	constant of Henry's law
h	heat transfer coefficient
J	stationary nucleation rate
K	constant
K^*	overall kinetic rate constant
k_B	Boltzmann constant
k_d	mass transfer rate
k_L	mass transfer coefficient
k_r	rate of absorption "reaction"
k_W	thermal conductivity of water
m	exponent
M_H	molecular weight hydrate
MW_W	molecular weight of water
N	average number of nuclei
n	building units
n	exponent
n^*	critical nucleus
n_{eq}	amount of dissolved gas at equilibrium
n^{tb}	amount of dissolved gas at turbidity
P	absolute pressure
P_{eq}	equilibrium pressure
q	exponent
r	particle radius
R	universal gas constant
Re	Reynolds number
S	supersaturation ratio
Sc	Schmidt number
T	absolute temperature
t	time interval
T_{bulk}	bulk water phase temperature
T_{eq}	equilibrium temperature
t_i	induction time of hydrate formation
V	volume
V_h	volume of a unit

W	work required for the creation of a nucleus
W^*	critical nucleus
x_b	mole fraction of gas in the bulk water phase in equilibrium
x_{int}	mole fraction of gas in the hydrate film in equilibrium
α_W	thermal diffusivity of water is
γ	overall order of the reaction
δ	liquid film thickness
$\Delta\mu$	gain of the volume free energy up changeover of one building unit
ΔE_a	apparent energy of activation
ΔG	excess Gibbs free energy
Δg_V	free energy change per unit volume
ΔS_e	entropy change upon hydrate formation
ΔT	supercooling
ΔV_e	variance from the volumes of water molecules
θ	contact angle
λ_H	hydrate dissociation heat
ρ_H	density of hydrate
σ_{ef}	effectual peculiar surface energy of the nucleus
$\sigma_{h/s}$	hydrate/solid interface
$\sigma_{s/L}$	solid/liquid interface
ϕ	distribution of hydrate particle size
ψ	coefficient
ΔG_S	surface excess Gibbs free energy
ΔG_V	volume excess Gibbs free energy
μ_0	0 th moment of the particle size distribution
μ_1	first moment of the particle size distribution
μ_2	second moment of the particle size distribution

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3 THE IDEAL SECOND MOMENT OF THE HYDRATES PARTICLE SIZE DISTRIBUTION

There are some differences between the scientific point of view and industrial approaches. For example, as discussed in the past chapter of the literature review, scientists considered differences in the fugacity of phases as the proper driving force, which implies pressure variations.

However, as pressure maintenance in pipelines is vital for companies, and determination of fugacity in different phases is challenging in practical situations, proposed models based on Englezos et al. (1987) kinetic model were abandoned in flow assurance issues instead of the primitive approach of Vysniauskas and Bishnoi (1983). Further simplifications of (Boxall et al., 2009) were used in flow assurance simulator packages (Schlumberger OLGA, 2016). On the other hand, models with temperature difference as a driving force were rejected by scientists due to a higher level of uncertainty (Meindinyo et al., 2015).

When hydrate particles are formed, the moment and the disseminate of the distribution of the formation of the hydrate particles are changed with time. In experimental techniques particle size analysis is vital it has a significant effect in the kinetics of gas hydrate formation and dissociation. Particle sizes can be measured experimentally by using classifiers (e.g., sieves), or they can be measured in-situ as discussed in the prior chapter. Table 3.1 listed some of well-known methods in methane hydrate particle sizes analysis.

Table 3.1 - Different method used for hydrate particle size analysis

Method	T/K	P/MPa	Particle size/ μm	Reference
FBR & MB	274–279	1.6–3.0	1–25	(Clarke; Bishnoi, 2005)
ND	230–263	6.2	200	(Sloan, 2003)
X-ray diffraction	233–273	1.0–1.5	150	(Takeya et al. 2000)
NMR	275	5.8	180–210	(Moudrakovski et al., 2004)

T : temperature, P : pressure, MB: material balance, ND: neutron diffraction, NMR: nuclear magnetic resonance and FBR: focused beam reflectance

Incidentally, it has been shown that the second moment of the particle-size distribution $\mu_2(t)$ is not only a key parameter in kinetic but in the slurry-flow containing hydrate. Predicting pressure drop because of the viscosity of the hydrate slurry (Mills, 1985; Uchida et al. 2003; Majid et al., 2018) is crucial in such a pipeline which is function of the particle-size distribution (Shi, et al. 2016) that is controlled by $\mu_2(t)$. Ancey and

Jorrot (2001) concluded that smaller particles result in a higher viscosity for a given shear rate and a solid fraction, as shown in Figure 3.1.

Figure 3.1 - The relative viscosities as a function of volume fraction for different mean particle size distribution (D_m).

Source: Adapted from Ancey and Jorrot (2001)

The vast majority of petroleum and natural gas engineers believe that most of the gas hydrates are formed due to a temperature drop caused by a valve or a choke suddenly leading to a pressure change, which is consequent of the Joule-Thomson effect (McCain, 2017). Kuang and coworkers (2019), concluded that in situations involving pipelines with high subcooling rate, the morphology of gas hydrate crystals has a geometry close to a circle (Figure 3.2).

While there is considerable diversity among the belief of scientists regarding hydrate crystallization process but eventually, all the models need to be fitted to experimental data of gas or water consumption versus time. For example, Englezos et al. (1987) assumed that the secondary nucleation rate is proportional to the second moment of the particle size distribution. However, they set the nucleation rate constant equal to 10^{-3} , which practically implies that there is no secondary nucleation due to crystal breakage.

Figure 3.2 - Morphology of the gas hydrate crystal growth at different cooling rates

Source: (Kuang et al., 2019)

It means that hydrate crystals are tiny, and therefore secondary nucleation is expected to be negligible during the time of the growth modeling. Herri et al. (1999) also suggested that secondary nucleation could not play a significant role in the crystallization of methane hydrate.

On the other hand, models developed by Bergeron and Servio (2008a); Bergeron and Servio (2008b) and Bergeron et al. (2010) declared that hydrate formation is a homogeneous nucleation phenomenon, and agglomeration, breakage and attrition are more likely to occur as particles reach considerable sizes. So, the secondary nucleation rate is proportional to the second moment of the particle size distribution and it is controlling the process.

However, Kashchiev and Firoozabadi (2003) mentioned that homogeneous nucleation for pressures less than 12000 kPa could only occur when the induction time is higher than 24 hours.

Some assumptions can be made to simplify the formula for evaluating the second moment of the particle-size distribution ($\mu_2(t)$). Since the solubility of guest gas is infinitely small in comparison to the amount of water in the cell, at induction time, while turbidity is occurring, there are uniform spherical seeds at reactor, whose volume and surface growth is rational to the amount of gas that has been solved at each time. Hence, all over the process, complete breakage and agglomeration will show their effects on the volume and surface of the uniform spherical seeds. So, considering that, the molar rate of water consumption may be expressed by the relation (Dalmazzone et al., 2009)

$$\frac{dn_w}{dt} = -v \frac{dn_H}{dt} = -vr_H \quad (3.1)$$

Where v is the hydration number of the hydrate. The molar rate of hydrate formation r_H is related to the rate of volume increase of the crystal, and finally to the linear growth velocity by

$$r_H = \frac{1}{\tilde{V}_H} \frac{dV_{cr}}{dt} \quad (3.2)$$

Where V_{cr} and n_H denote the volume and molar amount of gas hydrate, respectively, and $\tilde{V}_H$ is the molar volume of gas hydrate.

The rate of increase of the hydrate crystal volume can be expressed as follows:

$$\frac{dV_{cr}}{dt} = GA_{cr} = k_r (X_L - X_{H-L}) A_{cr} \quad (3.3)$$

Where G is the linear growth velocity of the hydrate crystal, A_{cr} is the crystal area, k_r is the kinetic growth constant of the methane hydrate crystal. Where X_L is the mole fraction of the guest gas in the bulk of aqueous phase at the experimental conditions (two-phase), as well as X_{H-L} is the solubility of the guest gas under hydrate-liquid water equilibrium (three-phase) at the temperature and pressure of experiment.

Although spherical geometry is the most favorable choice among engineers and scientists, it is possible to consider any other shape in evaluations. Some simple geometrical shapes and relations regarding their surfaces and volumes are listed in Table 3.2.

However, assuming that hydrate crystal has a spherical geometry, the crystal area (A_{cr}) is correlated with the crystal volume (V_{cr}) as follows:

$$A_{cr} = 4\pi \left(\left(\frac{3}{4\pi} \right) V_{cr} \right)^{2/3} \quad (3.4)$$

The crystal volume was proportional to the molar hydrate formation at the time of t (here is adding the amount of water to particle, so Equation 3.2 has a positive sign).

$$V_{cr} = \frac{n_{w,t}}{v} \tilde{V}_H \quad (3.5)$$

Combining Equations 3.1-3.5 leads to the following expression of the molar rate of produced hydrate

Table 3.2 - Different geometries that can be used for hydrate particle size shape

Shape	Regular form	Characteristic Length	Surface Area	Volume
Tetrahedron		edge	$\sqrt{3}a^2$	$\frac{\sqrt{2}a^3}{12}$
Cube		side	$6a^2$	a^3
Octahedron		side	$2\sqrt{3}a^2$	$\frac{\sqrt{2}a^3}{3}$
Icosahedron		side	$5\sqrt{3}a^2$	$\frac{5(3+\sqrt{5})a^3}{12}$
Dodecahedron		side	$3\sqrt{25+10\sqrt{5}}a^2$	$\frac{1}{4}(15+7\sqrt{5})a^3$
Truncated icosahedron		side	$\left(20\frac{3}{2}\sqrt{3}+\frac{5}{4}\sqrt{1+\frac{2}{\sqrt{5}}}\right)a^2$	$\left(\frac{125+43\sqrt{5}}{4}\right)a^3$
Sphere		radius	$4\pi a^2$	$\frac{4\pi a^3}{3}$

$$\frac{dn_H}{dt} = \frac{k_r}{\tilde{V}_H} (X_L - X_{H-L}) 4\pi \left(\frac{3n_{w,t}}{4\pi v} \tilde{V}_H \right)^{2/3} \quad (3.6)$$

Here the hydrate formation rate developed by Bergeron et al., (2010) can be applied

$$\frac{dn}{dt} = \frac{V_L \rho_w}{MW_w} (x_L - x_{H-L}) \pi \mu_2(t) k_r \quad (3.7)$$

Now equating Equation 3.6 to Equation 3.7 and canceling out parameters, the following expression for the second moment may result:

$$\mu_2(t) = \frac{MW_w}{V_L \rho_w v \tilde{V}_H} 4 \left(\frac{3n_{w,t}}{4\pi v} \tilde{V}_H \right)^{2/3} \quad (3.8)$$

To the best of our knowledge, this fascinating equation has passed unnoticed in the literature. This new relationship for the second moment of the particle size distribution

arising from this work opens a new door for future exploration of different frameworks. It is impressive that Equation 3.8 may be used as a useful tool for evaluation of the effects of promoters or inhibitors on the hydrate particle size. However, it should be noted that assumptions were entirely based on homogeneous formation and any breakage, agglomeration, or even secondary nucleation exist; they show their effects as spherical surface growth, so it is an ideal second moment of the particle-size distribution. A closer look at Equation 3.8 reveals that it is

$$\mu_2(t) = \underbrace{\frac{MW_W}{V_L \rho_W v \tilde{V}_H}}_1 \underbrace{4 \left(\frac{3n_{W,t}}{4\pi v} \tilde{V}_H \right)^{2/3}}_{\text{surface area of particle}} \quad (3.9)$$

Total volume of
Crystal

Which is a material balance-based equation.

In Equation 3.8, some parameters need to be determined and fitted to the experimental results.

- The molar weight of water (MW_W) is equal to 18.01528 g/mol.
- The density of water (ρ_W) can be calculated through the International Association for the Properties of Water and Steam (IAPWS) formulation (Wagner; Pruß, 2002).
- Hydration number (v) can be calculated through analysis of quadrupole point (Chapter 4).
- Molar volume of gas hydrates ($\tilde{V}$) can be calculated by MD simulation (Chapter 4).
- The number of moles of water used at each time ($n_{W,t}$) can be measured experimentally through conventional hydrate reactor by plotting the used amount of gas versus time multiplied by hydration number (Chapter 5).
- The total volume of water reacted (V_L) can be considered as a volume of water in the reactor.

Up to now the moments of distribution are introduced as the integral defined in equation 2.31 that here duplicated as Equation 3.10

$$\mu_2 = \int_0^\infty r^2 \phi(r,t) dr \quad (3.10)$$

And its value can be returned by solving systems of ordinary differential equations of Equation 2.38 that here duplicated as Equation 3.11

$$\begin{aligned}
\frac{d\mu_0}{dt} &= \alpha_2 \mu_2 & \mu_0(0) &= \mu_0^0 \\
\frac{d\mu_1}{dt} &= G \mu_0 & \mu_1(0) &= \mu_1^0 = 2r_c \mu_0^0 \\
\frac{d\mu_2}{dt} &= 2G \mu_1 & \mu_2(0) &= \mu_2^0 = 4r_c^2 \mu_0^0
\end{aligned} \tag{3.11}$$

For better understanding its concept, consider the systems of particles A and B shown in Figure 3.3:

Figure 3.3 - Comparison of two systems of particles

It is clear that the difference between these two systems cannot be distinguished by means of two first statistical metrics. However, the third one provides a general understanding of how these two systems of particles are behaving differently at a specific time.

Table 3.3 - Meaning of crystallization parameters versus statistics.

Statistic	Crystallization	System A	System B
Number of Population $\sum X_i$	0 th moment of the particle size distribution (μ_0)	5	5
Arithmetic average $\bar{X} = \sum X_i / n$	The first moment of the particle size distribution (μ_1)	10	10
Standard Deviation $\sigma = \sqrt{\sum (X_i - \bar{X})^2 / n}$	The second moment of the particle size distribution (μ_2)	$\sqrt{2} = 1.41$	$\sqrt{38} = 4.38$

So the parameter of the second moment of particle size distribution may imply how the society of particles is deviating from their average.

Herafter, throughout this document the reliability of the output of each mathematical model (Y^{calc}) against the experimental value (Y^{exp}) is assessed by using the parameters shown below (Heidaryan, 2019), being N_d the number of used data.

-The arithmetic average of the absolute values of relative errors (AARE%) is:

$$AARE\% = \frac{100}{N_d} \sum_{i=1}^{N_d} \left| \frac{Y_i^{exp} - Y_i^{calc}}{Y_i^{exp}} \right| \quad (3.12)$$

-The correlation coefficient R^2 , is defined as:

$$R^2 = 1 - \frac{\sum_{i=1}^{N_d} (Y_i^{exp} - Y_i^{calc})^2}{\sum_{i=1}^{N_d} (\bar{Y}^{exp} - Y_i^{calc})^2} \quad (3.13)$$

Small value of AARE% and an R^2 value close to 1.0 denote a good correlation.

Percentage of accuracy-precision (PAP) can be defined as:

$$PAP = 100 \left(1 - \frac{\sqrt{2}}{2} \sqrt{\left(\frac{1}{N_d} \sum_{i=1}^{N_d} \left| \frac{Y_i^{exp} - Y_i^{calc}}{Y_i^{exp}} \right| \right)^2 + \left(\sum_{i=1}^{N_d} (Y_i^{exp} - Y_i^{calc})^2 / \sum_{i=1}^{N_d} (Y_i^{exp} - \bar{Y}^{exp})^2 \right)^2} \right) \quad (3.14)$$

Nomenclature

$AARE\%$	arithmetic average of the absolute values of relative errors
A_{cr}	crystal area
G	linear growth velocity of the hydrate crystal
k_r	kinetic growth constant of the methane hydrate crystal
MW_W	molar weight of water
N_d	number of used data
n_H	molar amount of gas hydrate
PAP	Percentage of accuracy-precision
R^2	correlation coefficient
r_H	molar rate of hydrate formation
t	time
v	hydration number
V_{cr}	volume of gas hydrate (crystal)
$\tilde{V}_H$	molar volume of gas hydrate
V_L	volume of water reacted
X_{H-L}	solubility of the gas under hydrate-liquid water equilibrium (three-phase)
X_L	mole fraction of the guest gas in the bulk of aqueous phase (two-phase)
Y^{calc}	calculated value
Y^{exp}	experimental value
ρ^W	density of water
μ_0	0 th moment of the particle size distribution
μ_1	first moment of the particle size distribution
μ_2	second moment of the particle size distribution

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4 HYDRATION NUMBER AND MOLAR VOLUME OF GAS HYDRATES

4.1. HYDRATION NUMBER

The structure of CH₄ hydrate is a unit cell consisting of 46 water molecules. For hydrate composition, the hydration number is commonly used and defined as (CH₄ · ν H₂O) for CH₄ hydrate, where ν represents the mole number of water molecules reacted with a mole of CH₄ (Hydration Number). When the hydrate cavities are fully occupied by CH₄ molecules, ν approaches the ideal value of 5.75. However, since actual occupancies of CH₄ guest molecules into small and large cages are lower than unity, the hydration number at a specified condition must be determined. Here to calculate ν , enthalpy analysis at a quadruple point through equilibrium is used.

4.1.1 Experimental data

Details of experimental literature data for methane hydrate below the freezing point of water, the uncertainties in their measurements (u), the purity of the methane used in the experiments, and temperature range ($\Delta(T)$) are presented in Table 4.1.

Table 4.1 - Details of experimental literature data for methane hydrate equilibrium at low temperatures.

Reference	NDP	$\Delta(T)/K$	$u(P)/kPa$	$u(T)/K$	CH ₄ purity (%)
Roberts et al. (1940)	1	259	n.a.	n.a.	n.a.
Deaton and Frost (1946)	5	262.4-270.9	13.8	0.03	99.7
Delsemme and Wenger (1970)	8	82-100	0.01	n.a.	n.a.
Falabella and Vanpee (1974)	5	148.8-191.3	6.5	0.05	99.97
Makogon and Sloan (1994)	6	190.15-262.4	n.a.	0.1	99.9
Yang (2000)	1	259.1	n.a.	n.a.	n.a.
Hachikubo et al. (2002)	4	268.4-271.28	n.a.	n.a.	n.a.
Yasuda and Ohmura (2008)	11	244.2-272.2	20	0.2	99.99
Mohammadi and Richon (2010)	4	263.2-272.6	5	0.1	99.995
Fray et al. (2010)	6	145.75-195.74	1.2	0.05	n.a.
Nagashima Ohmura (2016)	7	197.3-238.7	1.8	0.15	99.99

NDP: Number of Data Points

Figure 4.1 presents an overview of these data. The experimental data obtained by Delsemme and Wenger (1970) is not displayed due to the very low temperature and pressure range of that data set. The trend presented by the experimental data is overall

the same, but some discrepancies are observed for the results by Fray et al. (2010) at low temperatures. Figure 4.1 also presents the results by Istomin et al. (2006) for molecular dynamics simulations (MD) for both hexagonal and cubic ice. For the same temperature, the equilibrium pressure is lower with cubic ice.

Figure 4.1 - Overview of experimental literature data for equilibrium conditions for methane, hydrate, and ice at temperatures below the quadrupole point. (Istomin et al. (2006) hexagonal ice: continuous line; Istomin et al. (2006) cubic ice: dashed line; Roberts et al. (1940): ■; Deaton and Frost (1946): ◆; Falabella and Vanpee (1974): ▲; Makogon and Sloan (1994): ●; Yang (2000): •; Hachikubo et al. (2002): ▼; Yasuda and Ohmura (2008): ★; Mohammadi and Richon (2010): ○; Fray et al. (2010): ×; Nagashima Ohmura (2016): +)

Source: (Heidaryan et al., 2019)

A likely explanation for the discrepancy observed by Fray et al. (2010) is the formation of cubic ice at lower temperatures. The possibility of hydrate equilibrium with supercooled water for methane was also presented by Istomin and coworkers (2006). Experimental evidence for methane hydrate in equilibrium with supercooled water was investigated by Melnikov et al. (2009). Their results are presented in Figure 4.2 and compared with molecular dynamics simulations by Istomin et al. (2006).

Figure 4.2 - Overview of experimental literature data for equilibrium conditions for methane, hydrate, and supercooled water at temperatures below the quadrupole point. (Istomin et al. (2006) supercooled water: continuous line; Melnikov et al. (2009): ▼)

Source: (Heidaryan et al., 2019)

4.1.2 Phase equilibrium modeling

Although new models (Chen and Guo, 1998) have been recently proposed to describe gas hydrate equilibrium, the most widely used approach is the van der Waals and Platteeuw (1959) (known as vdWP) equation. The vdWP model uses the Langmuir adsorption theory (Langmuir, 1918) to evaluate the chemical-potential difference of water in the metastable empty hydrate β -lattice and the hydrate lattice stabilized by the presence of guest molecules. The commercial package Multiflash (2014) uses the vdWP model combined with the Cubic-Plus-Association (CPA) Equation of State (Yakoumis et al., 1998) to predict hydrate phase equilibrium.

The vdWP model may fail when calculating cavity occupancy in multiple occupancy situations (Martín, A. 2010; Asiaee et al., 2013). This model has undergone several modifications to improve its performance (Parrish and Prausnitz, 1972; Holder et al.,

1980; Klauda and Sandler, 2000; Lee and Holder, 2002; Klauda and Sandler, 2003; Bandyopadhyay and Klauda, 2010).

The first notable improvement, however, was carried out by Parrish and Prausnitz (1972). These authors used a reference hydrate for which the chemical-potential difference could be determined from available experimental data for equilibrium at reference conditions.

This modification, in combination with the SRK-EOS (Soave, 1972), was used in the CSMHyd code (CSMHyd, 1998) and the PVTsim package (Calsep, 2011). Ballard and Sloan (2002) introduced further modifications to improve the performance of the vdWP approach. Their work is the backbone of the CSMGem code (Ballard and Sloan, 2004) for calculating hydrate formation conditions. Vinš and coworkers (Vinš et al., 2017) fitted the parameters of Ballard and Sloan (2002) model using highly accurate EOSs (Kunz and Wagner, 2012; Gernert and Span, 2016).

As seen in Figures 4.1 and 4.2, hydrate equilibrium pressures follow a logarithmic trend similar to that presented by the vapor pressures of pure substances. Therefore, representing the natural logarithm of hydrate pressure as a function of the reciprocal of absolute temperature at equilibrium condition may provide an appropriate description for the experimental data. Anderson (2004) used a quadratic equation to represent data along the coexistence line (ice, hydrate, and vapor) for methane hydrates based on this technique.

Figure 4.3 shows the hydrate pressure (in logarithm scale) as a function of the reciprocal of temperature along the equilibrium line for ice, methane hydrate, and vapor. The linear behavior is apparent. The experimental data can be fitted by the following Arrhenius-like equation:

$$P = \exp\left(A_1 + \frac{A_2}{T}\right) \quad (4.1)$$

Where P is pressure in kPa, and T is the temperature in K.

The data by Delsemme and Wenger (1970) was not considered in the fitting: they were considered just to evaluate the extrapolative capability of Equation 4.1. The resulting fit is presented in Figure 4.3, along with the results for Anderson's (2004) quadratic equation.

It can be seen that the correlation proposed correlates precisely the experimental data over the entire temperature range, with only two adjustable parameters. Moreover, the

extrapolation of Equation 4.1 for low temperatures results in a perfect prediction of the experimental data.

Figure 4.3 - Hydrate equilibrium pressure as a function of the reciprocal of temperature for methane, ice, and hydrate: experimental data and modeling. (Anderson (2004): continuous line; Equation 4.1: dashed line; data depicted in Figure 4.1: ■; Delsemme and Wenger (1970): ◆)

Source: (Heidaryan et al., 2019)

The same procedure was used to correlate the equilibrium pressures of supercooled water, methane hydrate, and ice, methane. The corresponding parameters are presented in Table 4.2.

Table 4.2 - Parameters A_i for Equations 4.1.

i	ice	supercooled water
1	1.58297×10^1	3.18030×10^1
2	-2.18367×10^3	-6.54584×10^3

The performance of Equation 4.1 can be seen in Figure 4.4; this Figure shows how the equilibrium curve with supercooled water deviates from the equilibrium curve with ice. The equilibrium curve with supercooled water can be extended down to 233.15 K,

which is the minimum temperature in which supercooled water exists (Armstrong, 2010). Melnikov et al. (2011) obtained experimental equilibrium conditions close to this limit. These data were not considered in the modeling but are presented in Figure 4.4. In this case, the experimental uncertainty is a long cue to the small hydrate samples, and the experimental data follow a different trend from data at higher temperatures. The intersection between the curves for the equilibrium with either ice and supercooled water is the quadrupole point. The calculated quadrupole point, considering Equation 4.1 for both equilibria, is 273.09 K and 2523.79 kPa. These values are in very good agreement with the values reported by Selim and Sloan (1989).

Figure 4.4 - Hydrate equilibrium pressure as a function of the reciprocal of temperature for methane, supercooled water, and hydrate: experimental data and modeling. (Equation 4.1 (ice): continuous line; Equation 4.1 (supercooled water): dashed line; Quadruple point: ■; Methane hydrate dissociation ($T < 253$) (Melnikov et al. 2009): ◆; Methane hydrate dissociation ($T > 253$) (Melnikov et al. 2009): ▲; supercooled water lower temperature limit: dash-point line)

Source: (Heidaryan et al., 2019)

Table 4.3 presents a comparison between the proposed equations and other well-known methods for the prediction/correlation of the equilibrium pressure of methane

vapor, ice, and the corresponding hydrate. The experimental data by Delsemme and Wenger (1970) was not considered in this calculation. Table 4.3 shows that the proposed Equation 4.1 is adequate to correlate the equilibrium data, and allows calculations more precise than any other method, regardless of its simplicity.

Table 4.3 - Comparison of different methods in the prediction/correlation of equilibrium pressure of methane, ice, and hydrate.

Method	AARE%	R ²	PAP
Equation (4.1)	4.23	0.9987	97.01
Multiflash (2014)	4.56	0.9987	96.77
Kunz and Wagner (2012) & Gernert and Span (2016)	4.79	0.9985	96.61
Anderson (2004)	5.26	0.9986	96.28
PVTsim (Calsep, 2011)	7.80	0.9949	94.47
CSMHYD (1998)	9.93	0.998	92.98
CSMGem (Ballard and Sloan, 2004)*	4.02	0.9972	97.15

* *Diverged at temperatures below 200 K (Results are for 70% of data).*

The prediction of equilibrium pressure through highly accurate equations of states such as GERG-2008 (Kunz and Wagner, 2012) and EOS-CG (Gernert and Span, 2016) is the number one choice of iterative methods. The results of Multiflash (2014) are more satisfactory in comparison with PVTsim (Calsep, 2011). The performance of CSMGem (Ballard and Sloan, 2004) is better than CSMHYD (1998). However, considering the necessity of a reasonable initial guess for the calculation, it easily fails to calculate the equilibrium pressure at low temperatures. This method can be used “in reverse”, in other words, to estimate the equilibrium temperature from the corresponding pressure. Due to the logarithm relationship, deviations in temperature are one magnitude order lower than pressure deviations. In any case, the calculations using Equation 4.1 result in better agreement with the experimental data than any other method. For the PVTsim method (Calsep, 2011), the equilibrium temperature could not be calculated for pressures below 110 kPa for methane hydrates.

Table 4.4 presents the values of AARE% for the prediction and correlation of equilibrium pressure and temperature of methane vapor and hydrate and supercooled water. Once again, the results of the proposed equations are superior to those obtained by other methods.

Table 4.4 - AARE% for the prediction of the equilibrium pressure of methane, hydrate, and supercooled water.

Method	AARE%
Equation (4.1)	1.62
Melnikov et al. (2009)	1.75

4.1.3 Enthalpy change of hydrate formation

The slope of the equilibrium pressure curve as a function of temperature is related to the enthalpy and volume change of any phase transition (Anderson, 2003) through the Clapeyron equation (Clapeyron, 1834):

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (4.2)$$

A reasonable approximation is to consider the volume change equal to the volume of the vapor in the equilibrium, which leads to the Clausius–Clapeyron (Clausius, 1850) equation:

$$\frac{d\ln(P)}{d(1/T)} = -\frac{\Delta H}{ZR} \quad (4.3)$$

The reliability of applying this equation to this equilibrium has been challenged (Anderson, 2003; Anderson, 2004) mainly because it ignores the amount of vapor dissolved in the water of equilibria. To provide a better insight into this issue, solubility of methane calculated along equilibrium lines with ice and with supercooled water through a high precision equation of state (Kunz and Wagner 2012; Gernert and Span (2016).

Using the compressibility factors of methane calculated from Setzmann and Wagner (1991), the enthalpy change can be estimated through the Clausius–Clapeyron (Clausius, 1850) equation. Figures 4.5 depicts the result of the current approach in comparison with values obtained from other methods for systems that contain methane hydrate.

Some concordance among experimental and calculated values does exist, but it is not perfect. For example, considering the equilibrium with methane, the experimental datum by Handa (1986) falls precisely on the calculated line, while the experimental datum by Rydzy et al. (2007) lies far from this line. Other calculated values, such as Yoon et al. (2003), Avlonitis (2005), and Anderson (2004) are rather scattered, without a definite trend.

The hydration number of hydrates can be estimated from the difference of enthalpy of hydrate dissociation in equilibrium with supercooled water and ice divided by the fusion enthalpy of water (Feistel and Wagner, 2006) at the quadruple point.

$$n = \left(\frac{\Delta H_{\text{supercooled water}}^{\text{hydrate}} - \Delta H_{\text{ice}}^{\text{hydrate}}}{\Delta H_{\text{liquid water}}^{\text{ice}}} \right)_{\text{@ quadruple point}} \quad (4.4)$$

The estimated value of the hydration number is 5.7 for methane. This value is close to the known value, which shows that the estimative provided by the proposed equations are reasonable.

Figure 4.5 - Enthalpy of hydrate formation for hydrates containing methane. (This study: continuous line; Handa (1986): ▼; Yoon et al. (2003): ■; Anderson (2004): ◆; Avlonitis (2005): ▲; Rydzy et al. (2007): ●)

Source: (Heidaryan et al., 2019)

4.2. MOLAR VOLUME OF GAS HYDRATES ($\tilde{V}$)

A unit cell of the cubic sl hydrate structure (lattice parameter of a unit cell is 11.87 Å) (Kirchner et al., 2004) consists of eight cavities (two 5^{12} cavities and six $5^{12}6^2$ cavities) that are formed by a three-dimensional network of 46 hydrogen-bonded water molecules, within guest molecules reside. For the molecular dynamics (MD) simulations of the current work, a cubic system consisted of $4 \times 4 \times 4$ unit cells ($47.48 \times 47.48 \times 47.48$ Å) with periodic boundary conditions (Kirov, 2003) was considered. Figure 4.6 shows the stable structure of the supercell of CH₄ clathrate hydrates of sl. The reported coordinates (Takeuchi et al., 2003) from X-ray diffraction analysis were used to construct this supercell.

Figure 4.6 The stable structure of the supercell of CH₄ clathrate hydrates.

The positions of oxygen molecules of the unit cell were obtained from the Weissenberg photograph (McMullan and Jeffrey, 1965), while the water oxygen atoms were acquired from sl structural obtained from X-ray diffraction experiments (Kirov, 2003). A single guest molecule placed at the center of each cage, corresponds to the case of full cage occupancy. Throughout the MD simulations, cage occupancy is kept fixed. Initially, *NVT* simulations with the Nosé thermostat algorithm (Nosé, 1984) were performed, and the systematic temperature is increased to equilibrium. Later *NPT* simulations with the Hoover barostat algorithm (Hoover, 1985) were run at equilibrium. Equilibration runs are performed for 0.2 ns, and the production run is analyzed for one ns, and a time-step of 1 fs (Essmann et al., 1995) is used; while thermostat and barostat relaxation times of 0.5 and 2.0 ps were used, respectively (Ning et al., 2015). Intermolecular interactions in the simulations were calculated with a cutoff distance of $R_{cutoff} = 12.0 \text{ \AA}$. The Coulombic long-range interactions were calculated with the particle mesh Ewald (PME) method considering a relative precision of 10^{-6} (Essmann et al., 1995). Accurate force field parameters are the key to obtain precise molecular structures. Force fields of TIP4P/2005 (Abascal and Vega, 2005) and TIP4PQ/2005 (McBride et al. 2009) were used to represent water molecules. The only difference between the two force fields is the magnitude of the charges. The OPLS-UA (Jorgensen et al., 1984) force field was used for modeling CH₄. Parameters for these force fields are presented in Table 4.5.

Table 4.5 - Potential parameters of the TIP4PQ/2005 (H₂O) (Abascal and Vega, 2005), TIP4P/2005 (H₂O) (McBride et al. 2009), and OPLS-UA (CH₄) (Jorgensen et al., 1984) models.

Force field	Atom	$\sigma(\text{\AA})$	$\epsilon/k_B(K)$	$q(e)$	Geometry	
TIP4PQ/2005	O	3.1589	93.2	0.0	$d_{OH}(\text{\AA})$	0.9572
	H	0.0	0.0	0.5764	$\angle H-O-H$	104.52
	M	0.0	0.0	-1.1528	$d_{OM}(\text{\AA})$	0.1577
TIP4P/2005	O	3.1589	93.2	0.0	$d_{OH}(\text{\AA})$	0.9572
	H	0.0	0.0	0.5564	$\angle H-O-H$	104.52
	M	0.0	0.0	-1.1128	$d_{OM}(\text{\AA})$	0.1577
OPLS-UA (CH ₄)	-	3.73	148.0	-	-	-

By evaluating the radial distribution functions (RDFs), it is possible to assess the ability of the model pairs to predict stable sl CH₄ hydrates. At the corresponding temperature

and pressure of equilibrium, the methane hydrate is stable (Heidaryan et al., 2019). RDF or $g(r)$, for oxygen-oxygen atoms, is shown in Figure 4.7 at equilibrium.

Figure 4.7 - The radial distribution function of oxygen-oxygen of the methane clathrate hydrates using TIP4PQ/2005 (Abascal and Vega, 2005), TIP4P/2005 (McBride et al. 2009) at equilibrium condition (275.15 K).

The peaks of $g_{oo}(r)$ are at approximately 2.8 Å, 4.5 Å, and 6.5 Å, which indicates the existence of tetrahedral hydrogen bonding structures of H₂O molecules in CH₄ hydrates (Chou et al., 2000). These results imply that force fields can describe the corresponding hydrate structures under conditions of hydrate stability.

At each temperature and pressure through using MD simulations and considering the following equation, volume of hydrate V is calculated

$$V \equiv \langle a \rangle^3 = \left\langle \frac{a_x + a_y + a_z}{3} \right\rangle^3 \quad (4.5)$$

Where the average lattice constant of the unit cell of sl methane hydrate denoted by $\langle a \rangle$. Thermal expansion coefficient (α_P) also can be calculated by differentiation ($a=V^{1/3}$) according to the following definitions:

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (4.6)$$

The NPT ensemble to calculate the thermal α_P of the single-crystal sl hydrates can be calculated through numerical differentiation of the fluctuations (Allen and Tildesley, 2017) as:

$$\alpha_P = \frac{\left(\langle V \cdot U \rangle - \langle V \rangle \cdot \langle U \rangle + P \left(\langle V^2 \rangle - \langle V \rangle^2 \right) \right)_{NPT}}{k_B T^2 \langle V \rangle} \quad (4.7)$$

All ensembled simulations were run using the LAMMPS MD simulation package (Plimpton, 1993). Classical MD simulations are neglecting quantum effects that are noticeable at low temperatures. The accurate determination of quantum correction is too intricate. Here the average temperature obtained by MD is rescaled to a temperature that includes the quantum effects. Calculated lattice constants, a , for methane from MD simulations as a function of temperature at the equilibrium pressure depicted (equilibrium pressure smaller than 100 kPa considered to be 100 kPa) in Figure 4.8.

Figure 4.8 - Calculated lattice constants, a , for methane from MD simulations and experimental data from literature as a function of temperature.

The result of TIP4PQ/2005 (Abascal and Vega, 2005), which is proposed for the path-integral, is always lower than reported values from TIP4P/2005 (McBride et al. 2009) and almost has a linear behavior. For the system with CH₄ as a guest, although the rescaling parameter was not used, TIP4P/2005 (McBride et al. 2009) returned excellent results and results from TIP4PQ/2005 (Abascal and Vega, 2005) are acceptable and in the range from the engineering point of view. For the system of methane, it is also obvious that by increasing temperature among MD simulation results and experimental data (Gutt et al., 2000; Kirchner et al., 2004; Ogienko et al., 2006; Takeya et al., 2006; Susilo et al., 2007; Takeya et al., 2010) result agreement is increasing.

As reported by Hansen and colleagues (Hansen et al., 2016) the experimental measurements for lattice constants of methane hydrate cleared that the partial cavity occupancy may affect the lattice constant (and ultimately its derivatives); however, it was also found to be insignificantly small if compared to the accuracy of experimental measurements. It was found 96.8% total cavity occupancy (as only the shortage is 12.9% in small cavities). This uncertainty also was proved in MD simulations (Costandy et al. 2016).

The polynomial fit to the temperature-dependent lattice constants of the hydrates sl is expressed as:

$$a(T) = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 \quad (4.8)$$

The term A_1 is set to zero to address the fact that the linear expansivity, $\partial a / (\partial T)$, needs to be zero at 0 K (Falenty et al., 2014). Polynomial coefficients of lattice constant fits are listed in Table 4.6.

Table 4.6 - Optimum parameters for the polynomial fit of the unit cell volume of the methane hydrate as a function of temperatures.

A_i	Constant
0	$1.1824 \times 10^{+01}$
1	0
2	4.3065×10^{-06}
3	-1.5568×10^{-08}
4	2.231×10^{-11}

Figure 4.9 shows the predicted results from Equation 4.7 and other well-known equations for the lattice constant of methane hydrate in comparison with experimental data described in Figure 4.8. Figure 4.9 reveals that while Equation 4.7 fitted very well

those equations proposed by Shpakov et al. (1998), and Hester et al. (2007) underestimate the lattice constant of methane hydrate. Equations attributed to Sun and Duan (2007) and Ogienko et al. (2006) appropriately fitted to data with temperatures below 200K, but for higher temperatures, both of them overestimate the lattice constant of methane hydrate.

Figure 4.9 - Predicted results from Equation 4.8 and other well-known equations for the lattice constant of methane hydrate.

Statistical parameters were used to evaluate the methods. Statistical parameters of different fitted equations are listed in Table 4.7.

Table 4.7 - Statistical parameters of different methods

Method	AARE%	R ²	PAP
Equation 4.7	0.044	0.9645	97.49
Shpakov et al. (1998)	0.213	0.9527	96.65
Sun and Duan (2007)	0.104	0.9497	96.44
Hester et al. (2007)	0.362	0.9495	96.42
Ogienko et al. (2006)	0.092	0.9371	95.55

Concerning the statistical parameters provided in Table 4.7, it is clear that the correlation developed is more than 97% reliable for the lattice constant of methane hydrate. As the magnitude variation of the lattice constant is not so large, all the models return acceptable numerical value, but superiority and consistency of Equation 4.7 is clear over other methods.

The thermal expansion coefficient of the fully occupied methane hydrate is shown in Figure 4.10. In this figure, filled points are given by fluctuations in the NPT ensemble (Equation 4.6), while unfilled symbols are from MD simulation, which was carried by Ning et al. (2015).

Figure 4.10 - The isobaric thermal expansion coefficient of sl hydrates as a function of Temperature. Result of the current study with reported values from Ning et al. (2015).

The simulation result of the current study is in agreement with the result from Ning et al. (2015). It can be seen that the isobaric thermal expansion coefficient has a linear behavior and almost linearly increases with increasing temperature.

The substitution of Equation 4.7 into Equation 4.5 returns below a simple tool for calculating α_P .

$$\alpha_P(T) = \frac{3(2A_2T + 3A_3T^2 + 4A_4T^3)}{A_0 + A_2T^2 + A_3T^3 + A_4T^4} \quad (4.9)$$

Coefficients are those that determined in Table 4.6.

Results of Equation 4.9 and substitution of literature developed correlations in Equation 4.6 are plotted in Figure 4.11. Comparison of Figure 4.10 and Figure 4.11 shows that MD simulation is proper in volume prediction but not perfect in energy calculations.

Figure 4.11 - The isobaric thermal expansion coefficient of sl hydrates as a function of Temperature.

Result of the Equation 4.9 and correlation from literature.

Nomenclature

$\langle a \rangle$	average lattice constant
A_1	constant
A_2	constant
A_3	constant
A_4	constant
H	enthalpy
k_B	Boltzmann constant
P	pressure
R	universal gas constant
T	temperature
u	uncertainties in measurements
U	potential energy
V	volume
Z	compressibility factor
α_P	thermal expansion coefficient
$\Delta(T)$	temperature range

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5 METHANE HYDRATE FORMATION KINETIC AND SOLUBILITY STUDY

The conventional study of hydrate kinetic is relevant in the determination of the parameters required to determine the second moment of the particle size distribution, according to model described by the Equation 3.8.

5.1. MATERIALS AND APPARATUS

Analytical grade methane (with a purity of 99.99 mol%, Arian Gas Company) was used as the guest molecules for hydrate formation. Distilled deionized water (resistivity of 18.24 M Ω -cm) was used to prepare all the experimental solutions.

The experimental apparatus consisted of a reactor of approximately 400 mL, built of Inconel 600 which contains one sapphire viewing window capable of withstanding pressures up to 70000 kPa as well as a supply vessel (2000 mL), a water bath, a refrigeration/heating circulator controlling by a PID controller to adjust the bath temperature with a stability of ± 0.1 K, as shown in Figure 5.1. The temperature and pressure inside the cell were monitored with a temperature transmitter probe (PT500) and a pressure transducer (OmegaDyne Model PX01). The expanded ($k=2$) uncertainty was estimated to be ± 0.02 K and ± 10 kPa, for temperature and pressure, respectively. The cell was also equipped with an analog barometer for safety purposes. One Acton Raman spectrometer (LS-785, Teledyne Princeton Instruments) and one multi-channel Raman were used in the set-up apparatus. A laser source of 532 nm (HR-TEC-532, StellarNet, Inc.) was applied to the solution for excitation with an incident laser power of 100 mW. Each Raman spectrum was measured by averaging two accumulations, each of which was measured over the 10 s of spectral integration time.

Acton Raman spectrometer was used with a center wavelength of 630 nm at a grating of 1800 g/mm. It was utilized with a relatively high resolution of 0.5 cm^{-1} over the range corresponding to methane dissolved in water, large and small cages occupied by methane in (Qin and Kuhs, 2013). This setting was focused on the measurement of the Raman signals at 2860-2940 cm^{-1} to analyze the cages of the formed hydrate. A multi-channel Raman spectrometer (probe of a Horiba, HR 800) was also used. To correlate the Raman spectra of water and the methane hydrate peak, the spectral range of the spectrometer was 834-3810 cm^{-1} . A spectral resolution of 2 cm^{-1} has been used (Ou et al., 2015).

Figure 5.1 - Schematic diagram of the experimental apparatus.

5.2. HYDRATE KINETIC STUDY

Before the experiment, the reactor was washed three times with pure water and then thoroughly dried. In all the entire experiments, both of the reactor and supply vessel were immersed in the insulated bath. At first, the reactor was charged with purified water. After the temperature stabilization of the gas and liquid phases, methane was injected. Once the temperature was stabilized, the solution was agitated using a six-blade Rushton turbine impeller with a rotational speed of 450 rpm to minimize resistance to both heat and mass transfer. During this time, the cell temperature and pressure were kept constant by the action of a refrigerator and a proportional integral derivative (PID) controller. As the gas in the reactor was consumed during hydrate formation, additional gas was automatically supplied from a supply vessel, and the moles of gas uptake over time were calculated from the pressure drop profile in the supply vessel with respect to the initial pressure. Figure 5.2 shows the pressure profile of the supply vessel and temperature of the system during the formation process ($P=4900$ kPa). The formation process was terminated by stopping the gas supply to the reactor and reached an overall hydrate conversion of 12% (in other words, when ~12% of the gas was converted into hydrate or time reached to 120 min). Then the reactor pressure was slowly decreased to a pressure of about 250 kPa above the equilibrium pressure. Then the gas in the supply vessel was also discharged, and the stirring was stopped at 150 kPa above the equilibrium pressure.

During hydrate formation, the consumed mole of gas data was obtained from the pressure variation in the supply vessel and by recording every 10 s over the experiment's intervals.

Figure 5.2 - The supporting vessel pressure and bath temperature (not the cell T) profile during the formation process.

The moles of gas uptake in the supply vessel was determined using Equation 5.1 in which V_{SV} , P_{SV} , and T_{SV} are the volume, pressure, and temperature of the supply vessel, respectively, while R is the universal gas constant. So, at any given time of t , the number of moles of gas consumed for hydrate formation in the cell was the difference between the number of moles of the gas at $t=0$ and at a specific time t , in the supply vessel

$$n = V_{SV} \left(\frac{P_{SV}}{ZRT_{SV}} \right)_0 - V_{SV} \left(\frac{P_{SV}}{ZRT_{SV}} \right)_t \quad (5.1)$$

Here, z is the compressibility factor which was calculated by Nasrifar and Moshfeghian (2001) equation of state (NM-EoS)

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - 2b^2} \quad (5.2)$$

As its performance in the prediction of methane volumetric properties is better than other conventional EoSs of Soave (1972) and Peng and Robinson (1976). In Equation 5.2

$$a = a_c \alpha \quad (5.3)$$

Where

$$a_c = 0.497926 \frac{R^2 T_c^2}{P_c} \quad (5.4)$$

$$b = 0.094451 \frac{R T_c}{P_c} \quad (5.5)$$

And

$$\sqrt{\alpha_{methane}} = 1 + 0.281209 \left(1 - \sqrt{\frac{T}{T_c}} \right) \quad (5.6)$$

In this EoS $T_c = 190.564$ K, $P_c = 4599.2$ kPa, and $R = 8.31451$ J/mol-K, as well as the parameter of Equation 5.6 is determined in this study concerning procedure by Heidaryan et al. (2019).

Figure 5.3 shows the performance of Nasrifar and Moshfeghian (2001) equation of state for prediction of saturation density of methane in comparison with Soave (1972) and Peng and Robinson (1976). The superiority of the NM-EoS is evident in this figure in the prediction of saturated liquid density.

Figure 5.4 shows the performance of Nasrifar and Moshfeghian (2001) equation of state in the estimation of the compressibility factor of methane as a function of reduced pressure ($P_r = P/P_c$) for different reduced temperatures ($T_r = T/T_c$) from 0.9 to 1.45.

Based on the obtained result presented in Figures 5.3 and 5.4, the reliability of the used number of gas moles can be assured due to pressure decline. The mole fraction of methane dissolved into the water was obtained from the pressure change and can be calculated with regard to the mole number of water in the system through Equation 5.7

$$x_{CH_4} = \frac{n_{CH_4}}{n_{CH_4} + n_{H_2O}} \quad (5.7)$$

Methane mole consumed at 276.2 K at different pressures of 3700, 4900 and 7100 kPa are shown in Figures 5.5, 5.6, and 5.7 for all entire processes from the beginning.

Figure 5.3 - Performance of Nasrifar and Moshfeghian (2001) equation of state in the prediction of saturation density of methane and comparison with of Soave (1972) and Peng and Robinson (1976).

Figure 5.4 - Data from NIST and predicted (Nasrifar and Moshfeghian, 2001) gas-phase methane compressibility factor as a function of reduced pressure with reduced temperature.

Figure 5.5 - Experimental number of methane consumed at $T = 276.2$ K and $P = 3700$ kPa (inserted figure has same axes units).

Figure 5.6 - Experimental number of methane consumed at $T = 276.2$ K and $P = 4900$ kPa (inserted figure has same axes unit).

Figure 5.7 - Experimental number of methane consumed at $T=276.2$ K and $P=7100$ kPa (inserted figure has same axes units).

Figure 5.8 - Experimental and fitted curves for different pressures of methane hydrate formation at $T=276.2$ K (data after induction time).

Regarding Figures 5.5, 5.6, and 5.7, it is possible to represent data after induction point by a linear equation for different pressures, as depicted in Figure 5.8. Figure 5.9 the natural logarithm of induction time is plotted as a function of reciprocal of pressure and fitted by a linear equation, which is summarized in the same figure. While there is a good relation among dependent and independent values in this figure, extrapolation of the linear fitted equation shows that at pressures about 28000 kPa (~4060 psia), induction time is less than a minute for the temperature of 276.2 K. It means that from flow assurance point of view, hydrate formation is an abrupt process in pipelines working at such conditions.

Figure 5.9 - Correlation between induction time and pressure.

As discussed earlier, the model presented by Kashchiev and Firoozabadi (2003) considered continuously nucleation during the process, which means that it accounts for proportionality between the induction time and the nucleation rate. As well as, the model assumes that progressive nucleation is taking place.

$$t_i = K \left(S(S-1)^{3m} \right)^{1/1+3m} \exp \left(\frac{B}{(1+3m)\ln^2(S)} \right) \quad (5.8)$$

In which K is a kinetic constant, S is the supersaturation, m is a number that relates to the growth type.

The thermodynamic parameter B is given by:

$$B = \frac{4c^3 v_h^2 \sigma_{ef}^3}{27k_B T} \quad (5.9)$$

Kashchiev and Firoozabadi (2003) assumed growth by volume diffusion of dissolved gas through a stagnant layer formed around the nucleus, then $m=1$, so that linearization will result in:

$$\ln \left(S^{\frac{-1}{4}} (S-1)^{\frac{-3}{4}} t_i \right) = \ln K + \frac{B}{4 \ln^2(S)} \quad (5.10)$$

Which is an appropriate relation for plotting induction times against supersaturation ratios. Whereby B and K can be obtained from a regression as the slope and the intercept.

The supersaturation ratio S is defined by

$$S = \left(\frac{f(P, T)}{f(P_{eq}, T)} \right) \exp \left(\frac{\Delta v_e (P - P_{eq})}{k_B T} \right) \quad (5.11)$$

Where f is the fugacity of methane in the gas phase, P is the system pressure, and P_{eq} is the equilibrium pressure corresponding to the system temperature T .

The fugacity of methane is calculated using the Nasrifar and Moshfeghian (2001) equation of state, and the equilibrium pressure of P_{eq} can be determined experimentally through the current setup or be calculated through van der Waals and Platteeuw (1959) three-phase flash which will be discussed in the next section. In the supersaturation ratio S equation (Equation 5.11) parameter Δv_e is

$$\Delta v_e \equiv v \times V_w - \tilde{V}_H \quad (5.12)$$

In which $v=5.7$ is hydration number (Heidaryan et al. 2019), $V_w=0.0299 \text{ nm}^3$ is the volume of a water molecule (Huang et al. 2013) and $\tilde{V}_H=0.224 \text{ nm}^3$ is methane hydrate unit cell volume (Equation 4.7). The intercept and the slope of the straight line are $K=420 \text{ s}$ and $B/4=0.22$, respectively (Figure 5.10).

These values of K and B are evidence of heterogeneous nucleation was happening. However, this should be noted that homogeneous nucleation occurs only rarely with

minimal times less than five ns (Sarupria and Debenedetti, 2012). In other words, when induction time is more than a full day long (24 hours).

Figure 5.10 - Dependence of the induction time on the supersaturation ratio for methane hydrate at different pressures.

Remembering new developed for relationship for the second moment of the particle size distribution (Equation 3.8):

$$\mu_2(t) = \frac{MW_w}{V_L \rho_w v \tilde{V}_H} 4 \left(\frac{3n_{w,t}}{4\pi v} \tilde{V}_H \right)^{2/3} \quad (5.14)$$

While all parameters determined to this end, the only remained parameter is $n_{w,t}$ which for cases in this work can be represented by a linear equation by fitting to experimental data after induction time.

$$n_{w,t} = n_{w,0} + (dn/dt)t \quad (5.15)$$

In this Equation, $n_{w,0}$ is the mole number of water used at turbidity time, and dn/dt is the slope of gas consumed line (as both values are represented for gas consumed, they need to be multiplied by hydration number). As it was shown in Figures 5.5, 5.6, and 5.7, determination of turbidity time and eventually $n_{w,0} (=v \times n_{g,0})$ will be complicated

by increasing pressure. Assuming full occupancy, the number of moles of methane dissolved at turbidity is given by (Bergeron et al., 2010):

$$n_{g,0} = \frac{m_W C_{P_W} \Delta T}{\Delta H} + n' \quad (5.16)$$

Where m_W is the mass of water in the cell, C_{P_W} is the heat capacity of water (Wagner; Pruß, 2002), ΔH is the heat of methane hydrate formation (assumed to be equal to hydrate dissociation) calculated from (Heidaryan et al., 2019b) Equation (4.3 and 4.1) and ΔT is the change in temperature measured at the onset of hydrate growth in the liquid phase of the crystallizer (from low pressure to high pressure vary from 0.7 to 1.3 K). This Increase in the liquid phase temperature at the onset of methane hydrate growth at 276.2 K and 4900 kPa has been shown in Figure 5.11.

Figure 5.11 - Increase in the liquid phase temperature at the onset of methane hydrate growth at 276.2 K and 4900 kPa.

The number of moles of methane in the bulk liquid phase (n^l) is obtained from the following experimental measurements as well as modeled through fundamental thermodynamic concepts.

5.3. *IN-SITU* RAMAN SPECTROSCOPY STUDY

Up to now determination of the host structure and degree of cage occupancy by different guest molecules (Tang et al. 2018), phase behavior (Kwak et al., 2018), kinetic studies on the formation (Truong-Lam et al., 2019) and inhibition of gas hydrates (Kim et al., 2014) has been done through using Raman spectroscopy. As Raman spectroscopy is not susceptible to interference from aqueous environments, it is appropriate for the study of aqueous and hydrate conditions. However, in most spectroscopic analyses (including Raman), small specimens are prepared, and specific parts are analyzed under particular conditions using an optical probe or a microscope (Trueba et al., 2012). Nevertheless, its applications in gas hydrate study are limited due to small-scale samples either removed from the bulk phase of the hydrate or free from a controlled environment. In this regard, *in-situ* Raman spectroscopy is used to obtain more practical information during hydrate formation and dissociation under agitation (Lee et al., 2015).

5.3.1 Methane solubility and hydrate cell characterization

It is challenging to get precise conditions at the low temperatures to conduct experimental measurements of methane solubility in water. To obtain the calibration curve for accurate solubility data, experiments were conducted using the relationship between the intensity ratio of the Raman peak of dissolved methane at 2910 cm^{-1} and OH symmetric band stretching at 3220 cm^{-1} (Figure 5.12) which here is for high pressure of 60000 kPa and temperature of 302 K at hydrate-free, stable phase.

Raman peak intensity or areas cannot necessarily be compared directly from one measurement to the next because they are affected by the optical path (Wopenka and Pasteris, 1987). However, peak ratios (which are independent of the optical path), exposure time, and other experimental factors, may be used to determine the relative concentrations or number of moles (Wopenka and Pasteris, 1987). The gas solubility

can be measured in relation to Placzek's polarizability theory (Sum et al. 1997), which could be written in a simple form (Ou et al., 2015) as

$$X_{CH_4} \propto \frac{I_{CH_4}^{2910}}{I_{H_2O}^{3220}} \quad (5.17)$$

Figure 5.12 - Raman spectra of dissolved methane and pure water in the range 2850–3750 cm^{-1} .

Figure 5.13 Raman intensities 3D-plot of the dissolved methane in water.

Data collected for the Raman intensities of the dissolved methane are plotted in Figure 5.13. The linear behavior of the Raman peak intensity for pressures below equilibrium pressure is obvious in this figure. For pressure above equilibrium pressure, it is apparent that it has a lower slope with regard to pressure. It should be noted that although the slope is decreasing here, which may imply in underestimation of solubility, Raman intensity in the bulk of water will change in the same manner due to the change of symmetric stretching affected by hydrate particles. So, it is reasonable that this lower slope is ignored as it is canceled out with its peers at bulk water. However, considering experimental peaks at 2910 cm⁻¹ for calibration caused an overestimation in the prediction of methane solubility. In the evaluation of Raman intensities plot (Figure 5.13) at pressures above equilibrium pressure, there are two abnormalities (dissolved peak) around 2905 cm⁻¹ and 2915 cm⁻¹, which corresponds to the large and small cage of sl hydrate but cannot be clearly detected by multichannel Raman probe.

To address this issue in a better way, Raman intensity at 6000 kPa is plotted as a function of Wave number (2903 cm⁻¹ to 2918 cm⁻¹) in Figure 5.14.

Figure 5.14 - Raman intensities plot of the dissolved methane in the water at 276 K and 6000 kPa.

Deconvolution of this peak through using three peaks showed that the peak at 2910 cm⁻¹ was boosted due to the effects of neighbor peaks. So, in the calibration curve, the purified peak position was considered.

Results for kinetic experiments (including induction time and hydrate conversion with Raman spectra) for methane hydrate formation is shown in Figure 5.15. Under a constant temperature of 276.2 K (and 4900 kPa), the nucleation point was determined at 30 min, and once hydrates were formed, the methane conversion data were collected throughout the time of hydrate growth.

Figure 5.15 - Raman spectra of methane in the transition from dissolved methane to methane hydrate

During hydrate formation, spectrometer data was collected every 60s through in-situ Raman spectrometers, and the results showed the presence of methane gas dissolved in the water ($2910\text{-}2911\text{ cm}^{-1}$) and methane hydrate sl (2905 and 2915 cm^{-1}) in specific regions, more precisely in Figure 5.16. The red, blue, and pink curves in Figure 5.16 show the intensities of the Raman peak signals for dissolved methane and methane hydrate in the induction period, nucleation point, and hydrate growth interval.

In the first step of the methane hydrate formation process, methane molecules entered the aqueous phase. During this period, the in-situ Raman spectra could be used to observe the process by which methane reached its maximum solubility in water successfully (the red curves in Figure 5.16).

Figure 5.16 - Time-dependent Raman spectra of methane hydrate formation

In the first step of the methane hydrate formation process, methane molecules entered the aqueous phase. During this period, the in-situ Raman spectra could be used to observe the process by which methane reached its maximum solubility in water successfully (the red curves in Figure 5.16).

In the first step of the methane hydrate formation process, methane guest molecules entered the aqueous phase. During this period, the in-situ Raman spectra could be used to observe the process by which methane reached its maximum solubility in water successfully, according to the red curves in Figure 5.16. After the induction period, the first observable Raman peak of methane gas trapped in the large and small cages of sl and started to appear at around 2905 cm^{-1} (I_L) and 2915 cm^{-1} (I_S).

Two interesting phenomena can be observed from these two curves. The first one is the intensity of dissolved methane peak (around $2910\text{--}2911\text{ cm}^{-1}$) reduced at induction time because of formed hydrate salting-out effect on methane solubility. Later one is comprehended by deconvolution of the blue curve. Through the deconvolution technique and concerning all other parameters are fixed. The intensity is the only parameter that determines the concentration of each compound. It could be concluded

that after the induction time, main of concentration is with the small cages of methane hydrate, as the key parameter here is I_L to I_S ratio (black curve in Figure 5.17) which always is less than three and suggests the possibility of predominant occupancy of small cages.

Figure 5.17 - The dissolved methane and cage intensity by an in-situ Raman (black line is the ratio of red to green).

Thus, individual trends of I_L and I_S must be analyzed with respect to the I_L/I_S ratio to compare the relative occupancy of each cage accurately (Lee et al., 2015; Truong-Lam et al. 2019).

Considering all the above-mentioned points, finally, the calibration curve is plotted in Figure 5.18. Linear correlation between I_{2910}/I_{3220} and methane mole fraction in the binary system of $\text{CH}_4+\text{H}_2\text{O}$ is evident in this figure. The points illustrated in this figure are the average of three measurements. However, due to the negligible standard deviation, the error bars were not represented.

Figure 5.18 - Mole fraction of dissolved methane (of CH₄+H₂O) versus Raman peak intensities ratio.

Result of dissolved mole fraction of methane in the water at 276.2 K, and a pressure range from 500 kPa to 7000 kPa are presented in Figure 5.19 while the result of modeling through two-phase flash for pressures below hydrate equilibrium (Rachford and Rice, 1952) and van der Waals and Platteeuw (1959) three-phase flash are also depicted in the same figure. In both flash approaches, Nasrifar and Moshfeghian (2001) equation of state was used. Its alpha function for water (Equation 5.18) fitted to water vapor pressure ($T_C = 647.096$ K and $P_C = 22064$ kPa) and binary interaction parameters were considered as $k_{ij} = k_{ji} = -0.6539$.

$$\sqrt{\alpha_{water}} = 1 + 0.714326 \left(1 - \sqrt{\frac{T}{T_C}} \right) \quad (5.18)$$

Flowchart of two-phase flash (for pressures below hydrate equilibrium) and van der Waals and Platteeuw (1959) three-phase flash are depicted in Figure 5.20.

In van der Waals and Platteeuw (1959) flash of Figure 5.20 the difference between water chemical potentials in empty hydrate and filled hydrate can be expressed by:

$$\Delta\mu_W^H = RT \sum_j v_j \ln \left(1 - \sum_i \theta_{i,j} \right) \quad (5.19)$$

This is the molar Gibbs energy of the empty hydrate lattice.

Figure 5.19 - Mole fraction of dissolved methane (CH₄+H₂O system).

Hypothetically solid phase containing pure water molecules linked by hydrogen bonds. The right side of the equation designates the stabilization of the unstable water lattice by the attendance of guest gas within the cavities of water. In this equation, R stands for the universal gas constant, T is representing the absolute temperature, and the number of cavities per water molecule for guest molecule j is denoted by v_j . Term $\theta_{i,j}$ in the equation, signifies the occupancy of a cage (the probability of finding a guest molecule of type j in the cavity of type i). In the vdWP three-phase flash, the cage occupancy may be computed from the fugacity, f_i , of the guest gas, and the Langmuir constant, $C_{i,j}$.

$$\theta_{i,j} = \frac{C_{i,j} f_i}{1 + \sum_i C_{i,j} f_i} \quad (5.20)$$

Using the cell potential theory of Lennard-Jones-Devonshire (Lennard-Jones and Devonshire, 1937), a connection describing $C_{i,j}$ in terms of the cell potential, may be used

$$C_{i,j} = \frac{4\pi}{kT} \int_0^r \exp\left(\frac{\omega(r)}{k_B T}\right) r^2 dr \quad (5.21)$$

Where r is the radius of the free cavity and $C_{i,j}$ is the guest–host interaction potential at a distance r from the center of the cavity. As well as, T is temperature, and k_B is Boltzmann constant.

Figure 5.20 - Comparison of Rachford and Rice flash versus van der Waals and Platteeuw flash

It has been suggested by (McKoy and Sinanoğlu, 1963) that the Kihara potential (Kihara, 1951) function, $\omega(r)$, is the best choice to replicate the interactions between guest gas and host molecules as

$$\omega(r) = 2z\epsilon \left(\frac{\sigma^{*12}}{R'^{11}r} \left(\delta^{10} + \frac{a}{R'} \delta^{10} \right) - \frac{\sigma^{*6}}{R'^5r} \left(\delta^4 + \frac{a}{R'} \delta^5 \right) \right) \quad (5.22)$$

where δ^N is calculated using the equation below:

$$\delta^5 = \frac{1}{N} \left(\left(1 - \frac{r}{R_j} - \frac{a}{R_j} \right)^{-N} - \left(1 + \frac{r}{R_j} - \frac{a}{R_j} \right)^{-N} \right) \quad (5.23)$$

In which z is the coordination number of the cavity, σ is the collision diameter ($\sigma^* = \sigma - 2a$), ε is the characteristic energy, and a is the radius of the spherical molecular core. Parameters ε , σ , and a are called the Kihara potential parameters. N is an integer equal to either 4, 5, 10, or 11. R_j is the radius of the cavity j . It should be noted that Equation (5.21) does not have an analytical solution. However, its value can be appropriately estimated through Monte Carlo Integration (Sugiyama, 2015).

By converting driving force to supersaturation ratio through (Equation 5.11), result of the second moment of the particle size distribution ($\mu_2(t)$) through developed Equation fitted to the polynomial equation and its returned values are plotted in Figure 5.21 as a function of time (t) and supersaturation ratio (S).

Figure 5.21 - Contour plot of the second moment of the particle size distribution as a function of supersaturation and time

Bergeron et al. (2010) studied the kinetics of methane hydrate formation using the particle size analyzer of Zetasizer Nano ZS particle size analyzer (Malvern Instruments) and concluded that the number of hydrate particles remains constant

during the early stage of crystallization. Since the reaction rate constant of hydrate formation is an intrinsic parameter independent of time, the experiments were conducted over approximately the first 15 min (~1000 sec.) of the growth stage, as the particles remain in the nanometer range. Figure 5.22 shows the results of Bergeron et al. (2010) concerning the particle size analyzed (blue points) as well as their reported error bars, while the red line is the result of the currently developed model of Equation 3.8.

Figure 5.22 - Experimental second moment of the particle size distribution at 278.9 K and 5559 kPa (Bergeron et al. 2010) versus Equation 3.8.

A good agreement between the currently developed model and experimental values reported by Bergeron et al. (2010) was obtained for the results plotted in Figure 5.22 for times less than 1000 sec. It can prove their conclusion that the time span in which the studies of kinetic are conducting is another crucial feature in determination, whether the hydrate particles number stand constant. So, agglomeration, breakage, and abrasion are more likely to happen as particles reach substantial sizes, which is not only a function of time but also of supersaturation.

Nomenclature

a	EOS constant
B	constant
b	EOS constant
c	shape constant
C	Third virial coefficient
C_{Pw}	heat capacity of water
dn/dt	slope of gas consumed line
f	fugacity
f_{eq}	equilibrium fugacity
H	enthalpy
I	intensity peak
K	constant
kB	Boltzmann constant
m	exponent
m_w	mass of water in the cell
MW_w	Molecular weight of water
n	number of moles
n	number of moles of gas
$n_{w,0}$	mole number of water used at turbidity time
P	pressure
P_C	critical pressure
P_{eq}	equilibrium pressure
P_r	reduced pressure
P_{SV}	pressure of the supply vessel
R	universal gas constant
R_j	radius of the cavity j
S	Supersaturation ratio
T	temperature
T_C	critical temperature
T_r	reduced temperature
T_{SV}	temperature of the supply vessel
v	hydration number
V	volume
V_h	hydrate volume
$\tilde{V}_H$	hydrate unit cell volume
V_L	volume of water reacted
V_{SV}	volume of the supply vessel
V_w	volume of a water molecule
x	mole fraction
Z	compressibility factor
z	coordination number of the cavity
ΔV_e	variance from the volumes of water molecules
ε	characteristic energy
ρ_w	density of water
σ	collision diameter
σ_{ef}	effectual peculiar surface energy of the nucleus
$\mu_2(t)$	second moment of particle size distribution

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6 APPLICATION OF MICRO-DIFFERENTIAL SCANNING CALORIMETRY IN METHANE HYDRATE DISSOCIATION

Gas hydrate dissociation kinetics is known to be strongly dependent on surface effects (Mokhtari et al., 2009) as hydrate crystals are an aftereffect of erratic polymer adsorption. The chemical structure of these molecules is scythed, so between these attachment sites, the water surface can be curved. It means that it can bend in one direction or the other, which has the effect of shifting the ice freezing and melting temperatures (the Gibbs–Thomson effect). The displacement is positive in the case of melting (the melting temperature is higher than the 0 °C) and negative in the case of freezing, which links to an interface curvature. This simple explanation (Celik et al., 2010) has the quality of being able to explain both the inhibiting (or anti-freeze) character and the existence of superheated ice crystals well above 0 °C. Figure 6.1 is an illustrative explanation of why the gas hydrate stands stable at temperatures above quadrupole temperatures.

Figure 6.1 - Patchy polymer adsorption at the interface between the hydrate phase and water. When temperature increases above quadrupole, the hydrate persists if its interface becomes curved (with the radius of curvature R) by the Gibbs-Thomson effect.

Source: Adapted from Broseta et al. (2017)

In this way for determination of interfacial curvature of R (approximately the distance between adsorption patches), the Gibbs–Thomson equation (Nasir et al. 2020) is defined as

$$R = \frac{4 \times T_{qp} \times \gamma_{HW} \times \cos(\theta)}{\Delta T \times \rho_H \times \Delta H_d} \quad (6.1)$$

Where T_{qp} is the quadrupole temperature 273.09 K (Heidaryan et al., 2019), γ_{HW} is the hydrate-water interfacial tension which considers being a fixed value of 0.032 J.m² for the system of methane hydrate and water, and ρ_H is the molar density of hydrate which consider being a fixed value of 0.01112 mole.m³ for the system of methane hydrate (Anderson et al., 2003). Assuming an unfrozen liquid layer (Clennell et al., 1999), then $\theta=0^\circ$, thus $\cos(\theta)=1$. In this Equation, there are two more parameters of ΔH_d and ΔT , which are dissociation enthalpy (J.mol⁻¹) and superheating temperature (equilibrium temperature minus quadrupole temperature, K), respectively.

Calorimetry is a particularly beneficial method in systems where a phase changes like in a hydrate formation or dissociation process. Comfort of procedure and the capability to produce beneficial thermal data caused the differential scanning calorimeter (DSC) a valued instrument in this domain. If the size of sample is tiny and it is pretended to measure very small heat changes, the micro-differential scanning calorimetry (μ DSC) is the most appropriate technique. The working principle is relied on the measurement of the temperature of a sample and reference. So, the essential heat to achieve a zero difference between the two is recorded as raw result. The fundamental of this method is described in detail by Le Parlouër et al. (2004). Here the μ DSC technology has been used to determine dissociation enthalpy and superheating temperature and their effects on R in Gibbs–Thomson Equation.

6.1. MICRO-DIFFERENTIAL SCANNING CALORIMETER APPARATUS

Although the reactor cell used in the prior chapter is an excellent choice for hydrate studies, there are several issues that make its use challenging. The first issue is pressurizing a cell with such a volume. Pressurization is carrying out through an ISCO 260d syringe pump and, even for medium pressures, it is necessary to have elevated pressure from the supply gas cylinder. For high pressures, depending on the nature of the gas, a gas booster may be required. The second issue is the safety of the cell. Such a cell still needs to be checked due to the risk of leak and explosion, so during tests after each series of experiments, new sets of O-rings and seals are needed. Finally, temperature scanning of such a setup is exceptionally challenging.

With regard to the mentioned points, the use of a μ DSC evo, Setaram Inc., is more convenient for calorimetric studies. However, the instrument was not created originally for high-pressure studies, but for atmospheric evaluations in the temperature range from 238.15 K to 383.15 K, with a resolution of 0.02 mW. A wider range of temperature can be achieved by the aid of a heating-cooling bath of Julabo F32-HE. Instead of using a high-pressure gas panel and HP compressor panel, an ISCO 260d syringe pump (260 indicates the internal chamber volume of the pump in ml) has been used, being its input directly connected to the gas cylinder. The output of the pump is connected to a high pressure, ultra-duty stainless steel grade 316 pipe with 1 mm of inner diameter. On the way to the μ DSC apparatus, the pipeline is connected to a 3-port valve, being one of the ports a system vent (for purging). Through a three-way joint, the next way is connected to high-pressure crucibles with a height equivalent to 19.5 mm and an internal diameter of 6.5 mm. Current modification is adequate to carry out experiments up to 20000 kPa (200 bars or $\sim$ 2900 psia) but with no corrosive material. The setup is shown in Figure 6.2.

Figure 6.2 - Schematic of the experimental setup for moderate-pressure analyses based on microcalorimetry

The pressure accuracy of this system is the accuracy displayed by the ISCO 260d syringe pump, which is 10 kPa. In the case of corrosive gases like carbon dioxide or hydrogen sulfide, a new set of pipelines and connections are required. The μ DSC

setup is equipped with highly sensitive sensors, namely class FRS, which are used for vulnerable biological systems. The heat flow during the cooling and heating cycle ($0.1 \text{ K} \cdot \text{min}^{-1}$) of produced methane hydrate at 5700 kPa is detected by the FRS sensor and illustrated in Figure 6.3. At the same time, its sensitivity (fluctuations in measurements) is noticeable.

Figure 6.3 - Heat flow during the cooling and heating cycle of methane hydrate at 5700 kPa (2.8 mg of water).

6.2. EXPERIMENTAL PROCEDURES

The difference in the amount of heat required to maintain the sample and the reference at nearly the same temperature during the experiment is measured as a function of temperature and registered. The hydrate dissociation curves obtained with μ DSC were characterized by the onset, peak, and endset points.

The setup was calibrated before performing experiments against three reference standards of the calibration substances, which are water (distilled and deionized), naphthalene (>0.985 Sigma-Aldrich), and n-Decane (>0.995 Sigma-Aldrich) under atmospheric pressure of nitrogen (>0.999).

Figure 6.4 shows the temperature and enthalpy calibration plot for reference fluids of water (Haywood, 1990), naphthalene (Andon and Connett, 1980), and n-Decane (Zwolinski et al., 1978). The thoroughgoing variance in the transition temperature and the latent heat from references was 0.15 K and 0.17 J.g⁻¹, respectively.

Hydrate nucleation and growth for pure water in a static system of the μ -DSC apparatus is limited as a result of mass transfer restrictions and needs a high sub-cooling degree, which can produce ice formation. Lee et al. (2014) used the method of multicycles of cooling-heating to obtain the maximum conversion of water into hydrate. Andre et al. (2014) applied an in-situ stirring system while it was working at pressures up to 20000 kPa. Mu and von Solms (2018) inserted three capillary tubes with a 2.3 mm diameter and 0.8 cm length into the sample crucible as a new option.

The use of a surfactant dry solution (DS) promotes gas hydrate formation. Thus, considering recipe by Fan et al. (2014), 46.25 g of sodium dodecyl sulfate (SDS) solution (Sigma Aldrich, 99% purity), 3.75 g of hydrophobic silica nanoparticles (Isatis Nano Company, 99.99% purity) and air were mixed in a high-speed blender (Fan et al., 2014). In the SDS-DS system, micro-droplets in range of 1-2 μ m were captured by

nanoparticles of hydrophobic silica and set aside isolated from each other (Figure 6.5). Detached SDS-DS was devoted to increase gas transport in the water-gas interfacial surface area, which resulted in hydrate nucleation and growth. Fortunately, since the additive was neither hydrophilic nor porous and negligible amount of it was added to water, the thermogram did not change (Figure 6.3).

Figure 6.5 - Diagram design of methane hydrate formation and decomposition in the SDS-DS system.

(A) SDS-DS droplets showing in methane phase, (B–C) growth of methane hydrate shell formed around surface of droplets, (D) freezing hydrate particles, aggregation of droplets after hydrate dissociation.

Source: Fan et al. (2014)

The μ -DSC cells and all pipelines were flushed through using an abrupt process of opening-closing the 3-port valve with the test gas (nitrogen for calibration and methane for hydrate experiments) to eliminate any remaining air at least three times at 150 kPa. After this step, test gas was injected in the reference cell and in the sample one until the wanted test pressure was reached, and the temperature program was then initiated. The tests were conducted under a program of temperature ramping. First, the temperature increased to 293.15 K and then decreased to 243.15 K at the rate of 0.2 K/min⁻¹, after keeping it constant for ten minutes at 243.15 K, then temperature was increased to 293.15 K at the rate of 0.2 K/min⁻¹. During heating, two endothermic peaks are detected (Figure 6.3), the first one at 273.1 K shows ice melting and the second at 282.4 K indicates hydrate dissociation. The quantity of heat needed to dissociate the hydrate sample may be computed by multiplying each point by time and integrating the endothermic peak area with respect to temperature; this can be done through the Gaussian quadrature method (Davis, 2018).

6.3. RESULTS AND DATA PROCESSING

The onset temperature is widely used for estimating equilibrium points (Menezes et al., 2019) since it represents the beginning of the thermal event, and it should not be influenced by the heating rate or sample mass. The peak temperature may be considered as an estimate when curves overlap, or the onset is not well-defined, although it does not strictly represent an equilibrium point.

Figure 6.6 shows changes in heat flow during the heating cycle. Locus of onset, peak, and endset in this endothermic peak is apparent. For all three experiments, there is a peak just before the valley which demonstrate recrystallization, and it is logical due to thermodynamically favorable condition for hydrate formation. For the tests at 3200 kPa and 5700 kPa used amount of water was 2.7 mg while for the 7500 kPa run, 2.9 mg of water was applied (0.03 mg of each sample was SDS-DS, which is negligible in calculations).

Figure 6.6 - The dissociation thermograms of methane hydrate at three different pressure conditions.

In Figure 6.7, the hydrate dissociation equilibrium point obtained from endothermic peak measurements through μ -DSC, as demonstrated in Figure 6.6, is compared with the calculated values by van der Waals and Platteeuw (1959) three-phase flash and

Nasrifar and Moshfeghian (2001) equation of state. This approach gives the hydrate-liquid water- vapor (H-Lw-V) three-phase equilibrium boundaries accurately. As it is clear from Figure 6.7, the μ -DSC measurements are in good agreement with the analytical model calculations. In addition, this also demonstrates and confirms that the μ -DSC can provide accurate H-L-V equilibrium data for the slightly soluble gases even at medium pressure, although there are either thermal and mass transfer resistance. Another useful information regarding μ -DSC is that the endset points can be used as a hydrate risk area in flow assurance.

Figure 6.7 - Comparison of hydrate dissociation equilibrium data from the μ -DSC measurements and from the analytical model.

The following two equations can denote the dissociation reaction of hydrates to gas and water or ice:

Where v is the hydration number, which is 5.7 in methane hydrate (Heidaryan et al., 2019), and M is a hydrate forming gas (or hydrate-forming gas mixture). Definitely

These two reactions have different enthalpy, which the difference is the ice fusion enthalpy.

While Equation 6.3 is the objective of hydrate washing studies (Falenty et al., 2014), Equation 6.2 deals with hydrate dissociation enthalpy assuming hydrate is converting to gas and liquid water.

The critical parameter to calculate the dissociation enthalpy of hydrate is the determination of the mass of reacted water converted into hydrate and the mass of free water or ice in the sample. From the endothermic peak area of ice melting using an ice melting enthalpy, the precise amount of free water, m_i , can be computed:

$$m_i = \frac{Q_i}{333.25} \quad (6.4)$$

Where Q_i is the amount of heat that is released during ice melting, and it may be calculated from the endothermic peak area of ice melting. Hence, the enthalpy of hydrate dissociation per mole of producing gas, ΔH_d , can be calculated by:

$$\Delta H_d = \frac{Q_h \times M_w \times v}{m_t - m_i} \quad (6.5)$$

Where m_t is the total mass of water in the sample cell, M_w is the molar mass of water. The amount of heat absorbed in the hydrate dissociation process, Q_h , also needs to be computed by integrating the endothermic peak area of hydrate dissociation. According to Circone et al. (2005), the hydration number is considered to be constant if pressure is less than 9700 kPa. It should be noted that in this approach the returned enthalpy value is based on the assumption that the formed solid is constructed of two separate parts of ice and hydrate. So, in the first step, ice is melting and then hydrate. However, clearly, after ice melting due to favorable hydrate formation conditions, sometimes there is recrystallization just before hydrate dissociation onset, which caused an overestimation in reported values.

It is possible to calculate the dissociation enthalpies of hydrates by applying the Clapeyron equation (Clapeyron, 1834). Suggested by van der Waals and Platteeuw (1959), the Clapeyron equation can be used to calculate the dissociation enthalpy of the clathrate hydrate along from the slope of the three-phase line and the change in molar volume as

$$\frac{dP}{dT} = \frac{\Delta H_d}{T \Delta V} \quad (6.6)$$

Where T and P are the absolute temperature, and absolute pressure, ΔV is the molar volume change due to the phase transition from hydrate to water and gas, that can be computed by:

$$\Delta V = \left(1 - \frac{vX_G}{1 - X_G} \right) V_G + vV_w - V_H \quad (6.7)$$

In which V_G , V_W , V_H are the molar volume of gas, water, and hydrate, respectively. As well as, X_G is the mole fraction of dissolved gas, and v is hydration number. Substituting Equation (6.7) into Equation (6.6), will result in explicate expression for hydrate dissociation enthalpy as

$$\Delta H_d = T \times \left(\left(1 - \frac{vX_G}{1 - X_G} \right) V_G + vV_w - V_H \right) \frac{dP}{dT} \quad (6.8)$$

The methane molar volume can be obtained using Nasrifar and Moshfeghian (2001) equation of state, the water molar volume can be obtained using (IAPWS) formulation (Wagner; Pruß, 2002), V_H can be obtained using Equation (4.7), and dT/dP can be calculated using van der Waals and Platteeuw (1959) three-phase flash.

Experimental result of methane hydrates enthalpies of dissociation of current experiments and experimental results of Gupta et al., (2008) and Mu and von Solms (2018), as well as calculated values of Equation 6.8, are illustrated in Figure 6.8. Clearly, all experimental results (all here are results of different μ -DSC studies) are slightly higher than the returned value of the analytical model. According to Lee et al. (2013), this value for temperatures below 285 K can be represented as a single valve. An average of all experimental measurements, 55 kJ.mol⁻¹ of methane is suggesting here.

Figure 6.9 plotted curvature radius R as a function of equilibrium pressure. While it is logical that by increasing pressure, the curved surface effect intensified ($1/R$), it is also a good benchmark for measurements in porous media or even small sample holders that how the media affect the measurements. It is interesting also that a slight anomaly in order of 0.1 μm needs several degrees of superheating to be a flat surface.

Figure 6.8 - The enthalpies of dissociation of methane hydrate, experimental values, and calculated result of Equation 6.8.

Figure 6.9 - Curvature radius R as a function of equilibrium pressure.

6.4. HYDRATE DISSOCIATION KINETIC MODEL

Kim et al. (1987) proposed a model to evaluate the kinetics of methane hydrate dissociation, which was based on experiments in a semi-batch stirred-tank reactor. Hydrate decomposition was carried out by reducing the pressure on hydrate slurry under constant temperature. They assumed that the overall course of hydrate dissociation involved two significant stages of

- 1) destruction of the water clathrate lattice at the surface of a particle
- 2) desorption of the methane (guest molecule) from the surface

while all happened at the solid surface, not inside the bulk of the solid, and the dissociation rate is proportional to the existing driving force. The proposed model (Kim et al. 1987) linked the dissociation proportion with the difference in fugacity of methane at equilibrium pressure and the experimental pressure multiplied by hydrate particle surface area as

$$\frac{-dn_H}{dt} = k_d A_s (f_{eq} - f) \quad (6.9)$$

While literally, it is a mirror form of the model proposed by Englezos et al. (1987), in which same conditions of no heat and mass transfer resistance were also assumed. The driving force in this approach is determined as the difference between the fugacity of methane at the equilibrium, f_{eq} and the fugacity of methane at the gas state, f . The overall form of equation declare that the rate of hydrate dissociation is relative to the combined surface area of the dissociating particles, A_s and dissociation rate constant, k_d . The parameter A_s , was stated as a function of n_H with the next simplification assumptions:

- (1) The hydrate is constant in conformation and structure, as well as contains ρ_H moles of methane per unit volume;
- (2) The same volume and a uniform dissociation rate for all particles is assumed;
- (3) The number of particles does not become diverse during dissociation;
- (4) The particles are spheres (but they can be varying by sphericity factor);

(5) The same diameter of D_0 before dissociation for the hydrate particles at begins is considered; Taking into account all the above simplifications, the dissociation proportion equation can be simplified to:

$$\frac{-dn_H}{dt} = k \times n_0^{1/3} \times n_H^{2/3} \quad (6.10)$$

$$k = k_d \left(\frac{6}{\psi \rho_H D_0} \right) (f_{eq} - f) \quad (6.11)$$

In which ψ is a factor of the sphericity. Here the rate constant, k has the dimension of reciprocal of time. By combining temperature dependence of Arrhenius type function into the rate constant, the constant rate k can also be stated as follows:

$$k = k_0 e^{-\Delta E/RT} (f_{eq} - f) \quad (6.12)$$

Where k_0 is reliant on the initial particle geometry, but it is independent of the temperature and pressure.

The intrinsic dissociation rate constant, k_0^d which is independent of the temperature, pressure, and particle geometry, is obtained from:

$$k_0^d = k_0 \left(\frac{\psi \rho_H D_0}{6} \right) \quad (6.13)$$

However, the geometry and size of the hydrate particles could be appraised, as the size and geometry dimension of hydrate particles was not obtainable in the laboratory. By assuming spherical shape ($\psi=1$), they estimated this parameter from a force equilibrium in the Stokes flow region with delayed settling time measured as

$$\frac{\psi \rho_H D_0}{6} = 2.12 \times 10^{-2} \quad \text{mol.m}^{-2} \quad (6.14)$$

So, the size of the particle was calculated to be about 16 μm . The experimental kinetic data were fitted using a non-linear least-squares method, and the intrinsic dissociation rate constant was calculated to be $1.24 \times 10^9 \text{ mol.m}^{-2}.\text{kPa}^{-1}.\text{s}^{-1}$ with activation energy ΔE determined as 78300 J.mol^{-1} although the heat of formation of the methane hydrate is around 62800 J.mol^{-1} of methane (Makogon et al., 1997). The two values are comparable.

Clarke and Bishnoi (2001), assumed that there is no breakage or agglomeration during the decomposition and used the homogeneous population balance equation

$$\frac{\partial \phi}{\partial t} + \frac{\partial (G\phi)}{\partial r} = 0 \quad (6.15)$$

Solving it simultaneously with Equations 6.9, the following expression is obtained:

$$n(t) = n_0 - \frac{\pi}{\psi} k_d V (f_{eq} - f) \left(\frac{1}{3} \mu_0^0 G^2 t^3 + \mu_1^0 G t^2 + \mu_2^0 t \right) \quad (6.16)$$

$$G = \frac{k_d M_w (f_{eq} - f)}{3 \rho_H} \frac{\phi_S}{\phi_V} \left(\frac{6 \phi_V}{\pi} \right)^{2/3} \quad (6.17)$$

Where ϕ_S and ϕ_V are surface and volume shape factor; however, applying this model needs an external online particle size analyzer apparatus.

In the current study, it is assumed that hydrate crystal has a spherical geometry (Dalmazzone et al., 2009). Thus, in Equation 6.10, the surface area of the decomposing particles is correlated with the crystal volume (V_{cr}) as follows:

$$A_S = 4\pi \left(\left(\frac{3}{4\pi} \right) V_{cr} \right)^{2/3} \quad (6.18)$$

The crystal volume is proportional to the molar hydrate dissociated at time of t

$$V_{cr} = \frac{n_{total} - n_t}{V} \tilde{V}_H \quad (6.19)$$

Where n_{total} is the total number of water moles that formed hydrate and n_t is the number of moles of hydrate that dissociated. From μ -DSC (remember Equation 6.5) it can be deduced the total number of water moles that formed hydrate and the molar amount of dissociated hydrate

$$\frac{n_{total} - n_t}{V} = \frac{Q_{total} - Q_t}{\Delta H_d} \quad (6.20)$$

Substituting Equation 6.20 into Equation 6.19 and then 6.18, now Equation 6.9 is transformed into Equation 6.21:

$$\frac{-dn_H}{dt} = k_d 4\pi \left(\left(\frac{3}{4\pi} \right) \left(\frac{Q_{total} - Q_t}{\Delta H_d} \right) n_w \tilde{V}_H \right)^{2/3} (f_{eq} - f) \quad (6.21)$$

While the applied temperature of hydrate dissociation is less than 285 K (Mokhatab and Poe, 2015), the unique value of 55 kJ.mol⁻¹ of methane can be used. As well as to avoid numerical integration of the μ -DSC endothermic peak, its value can be fitted by a Gaussian equation (Ingster and Suslina 2012), which can be analytically integrated for the required values. Here it is necessary that full-time peak obtained from the μ -DSC thermograms (onset to end set) be unit scaled with the decomposition time, and the only parameter in this model is k_d that could be fitted to experimental data of dissociation process. The fugacity of methane is calculated by Nasrifar and Moshfeghian (2001) equation of state according to the prior chapter.

To evaluate the performance of the proposed model, produced methane hydrate in the previous chapter were decomposed at a temperature of 276.2 K under different pressures of 2700 kPa, 2900 kPa, and 3200 kPa with 450 RPM to minimize heat and mass transfer resistance. As recommended by Jarrahan and Heidaryan (2014), the endpoint of each reaction is determined by the time when no more gas is produced and confirmed by Raman peak. Figure 6.10. shows the performance of Equation 6.21 and Kim et al.'s (1987) model in the prediction of the experimental mole ratio of methane hydrates during decomposition. Raman spectra of the endpoint of decomposition at 3200 kPa is also showed in this figure. The better agreement of the current approach over the model proposed by Kim et al. (1987) is evident in Figure 6.10, that shows the ratio of decomposed hydrate mole (n_H) to the initial mole of hydrate (n_0) as a function of time.

Figure 6.10 - Mole ratio of methane hydrates during decomposition experimental and modeling.

Nomenclature

A_s	combined surface area of the dissociating particles
D_0	hydraulic diameter
f	fugacity
f_{eq}	equilibrium fugacity
k	rate constant
K_0^d	intrinsic dissociation rate constant,
k_d	dissociation rate constant
MW_w	molar mass of water
n_H	hydrate mole decomposition
P	pressure
Q_h	hydrate dissociation process absorbed heat
Q_i	amount of heat released
R	interfacial curvature
T	temperature
T_{qp}	quadrupole temperature
V_G	molar volume of gas
V_H	molar volume of hydrate
V_W	molar volume of water
X_G	mole fraction of dissolved gas
γ_{HW}	hydrate-water interfacial tension
ρ_H	molar density of hydrate
ϕ_S	surface shape factor
ϕ_V	volume shape factor
ψ	sphericity factor
ΔH_d	dissociation enthalpy
ΔT	superheating temperature
ΔV	molar volume change
μ_0	0th moment of the particle size distribution
μ_1	first moment of the particle size distribution
μ_2	second moment of the particle size distribution

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7 CONCLUSIONS AND RECOMMENDATIONS

Scientific conclusions achieved in this study can be reflected as:

1. Hydration number of gas hydrates can be calculated accurately by analysis of dissociation enthalpy at quadrupole point.
2. Molecular dynamics (MD) simulations can be effectively used as a technique to determine the volumetric properties of gas hydrates, while here, the molar volume and the isobaric thermal expansion coefficient of methane hydrate were calculated with this tool.
3. The solubility of methane in water is a crucial parameter for both kinetic and flow assurance studies concerning hydrates. This parameter was measured here successfully through Raman spectroscopy and was modeled analytically by two and three-phase flash applying a cubic equation of state.
4. The ideal second moment of the hydrates particle size distribution can be calculated for the methane as it is slightly soluble in water through a material balance equation.
5. Plotting reciprocal of induction time versus the logarithm of pressure can determine a warning for flow assurance purposes.
6. While conventional reactors are necessary for hydrate formation and decomposition studies, HP- μ DSC is a useful tool and provides better insight due to providing temperature scanning of the under-evaluation system.
7. From the day that first work concerning kinetic of hydrate got published, none of the models are able to cover a full understanding of the physics behind the phenomena. Still, all of them are useful and extend the insight of researchers, and always there is a room for improvement.

Finally, due to Brazilian deep-water resources investigation on kinetic on natural gas hydrate, it is suggested to continue studying the effects of other hydrocarbons, inhibitors, and natural electrolytes.