Framework for clathrate hydrate flash calculations and implications on the crystal structure and final equilibrium of mixed hydrates

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ABSTRACT

Clathrate hydrates, usually called gas hydrates, are compounds of great interest in oil industry, as well as in gas separation and storage, water purification etc … Like many other compounds that phase change, in this case from liquid water to non stoichiometric crystalline compound, modeling is required to understand and optimize the processes that involve them.

Therefore, the classic thermodynamic equilibrium model is combined with mass balance calculations during gas hydrate crystallization. Two frameworks for performing clathrate hydrate thermodynamic flash calculations at constant volume are presented and compared to experimental results at low crystallization rate. The inputs are the quantity of mass (water and gas molecules), and the volume. The variable is temperature (three phases thermodynamic flash at a given temperature), while the volume is kept constant.

The first framework suggests that the hydrate phase is growing at local thermodynamic equilibrium, without any reorganization of its content of the occupancy of the cavities. In the second framework, the hydrate phase can reorganize itself during growth (locally or completely). These frameworks are investigated, as well as the impact of the Kihara parameters uncertainties.

These frameworks calculate well the final pressure, hydrate composition. In addition, the hydrate volume and mole amount in each phase is provided with reasonable accuracy. Note: uncertainties on the final pressure and hydrate volume are below 5%. Moreover, the results are quite sensitives to the value of the Kihara parameters, demonstrating the importance of their values for a given computer code.

This work provides a more realistic and comprehensive view of gas hydrate crystallization.

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1. Introduction

Clathrate hydrates (also called gas hydrates) are crystalline water-based solids that resemble water ice, in which small molecules (typically gases) are trapped inside cavities of hydrogen bonds. They form under high pressure (few to tens Mpa) at low temperature (usually under 20 °C), and cover vast areas of the ocean floor for example. These gas molecules, or guest molecules, are captured in these cavities. These cages are stabilized by van der Waals forces. Thanks to these forces, the clathrate hydrate structure is made possible. Note that recently Falenty et al. [12] managed to form empty SII clathrate hydrates at 145 K.

As crystals, different polymorphic forms are known and were studied in the past [32]. There are three main structures: SI, SII and SH, composed of different kind of cavities, surrounded by differing polyhedra sharing faces. Jeffrey [19] suggested the nomenclature e^f to describe the polyhedra (where e is the number of edges, and f the number of faces). The polymorphic forms exhibit different densities with differences in terms of thermodynamic equilibrium. Most important, the kind of guest molecules impacts the polymorphic form to be crystallized. In addition, for a given gas mixture, the occupancy of the cavities is not stoichiometric.

Clathrate hydrates are an crucial issue in many fields, from oil & gas industry [6,26], to carbon capture and storage [9], air conditioning [8], or even planetary science [15]. They have an enormous potential as an energy resource because of the tremendous quantity of methane trapped within them [21]. Understand that hydrate plugs in deep-sea pipelines probably pushed the worldwide study of clathrate hydrates into being. Hydrate management, or "flow assurance", in the petroleum industry is a complex technical

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challenge. Hydrate plugs can have catastrophic consequences, stopping the oil production for days or weeks, with the difficulty of dissociating the hydrate crystals. There are many solutions to this problem, such as kinetic or thermodynamic additives, or just employing avoidance techniques [31]. In the case of kinetic additives, the aim is to slow down the hydrate nucleation and growth (KHI, for "Kinetic Hydrate Inhibitor"), or to avoid agglomeration (AA, for "Anti-Agglomerant"). In thermodynamic additives (usually alcohols, such as methanol), the objective is to change the thermodynamic equilibrium itself, and avoid the hydrate zone.

To investigate hydrate avoidance, and/or thermodynamic inhibitors, both the understanding of the thermodynamics and the crystallization mechanisms of clathrate hydrates are required. While a thermodynamic model exists to simulate clathrate hydrate liquid–solid equilibrium, there is a major issue in modeling complex situations (such as flow assurance). Moreover, the quantity of kinetic inhibitors to avoid the hydrate formation in a pipe is dependent on the volume of crystal to be formed. So, there is a request to know "when", and "how many".

The thermodynamic modeling gives the final state of a system. Usually, this final equilibrium is enough for the modeling of chemical processes, since the thermodynamic path does not matter. In the case of clathrate hydrates, non-stoichiometric compounds are studied, and there is a question about the role of the thermodynamic path. It could matter in this specific case since different mechanisms need to be considered. In our study, many parameters are taken into account: gas consumption that changes the gas composition, and hence the thermodynamic equilibrium; molecules enclathration in the crystal characterized by the occupation of cavities (driven by thermodynamics or kinetics [23]).

Hence, it is crucial to understand clathrate hydrate crystallization to model the local change over time of the hydrate composition during crystal growth. At the end of the crystallization, whatever the topic (flow assurance, carbon capture and storage, planetary science …), the modeling of clathrate hydrate equilibrium and crystallization is key to develop process simulation and sizing. Especially because the volume of the final crystal phase and the amount of gas captured is a essential result to predict. For this purpose, the methodology can be a thermodynamic or kinetic. A kinetic model, incorporating crystal growth, was recently suggested by Herri and Kwaterski [16]. More recently, a kinetic flash algorithm has been suggest by Boesen et al. [3], based on the Skovborg model [29].

In the present approach, a thermodynamic method was chosen, combined with mass balance calculation, that is to say a thermodynamic flash approach for clathrate hydrates. For this endeavor, some assumptions are needed to take into account the molecules' enclathration. Either the hydrate is growing at local thermodynamic equilibrium, or the whole crystal phase is at thermodynamic equilibrium. So, the two assumptions are considered within a flash calculation.

Our objective is to present two frameworks for the clathrate hydrate thermodynamic flash calculations at constant volume. By presenting to differing frameworks, three kinds of calculations are available: two at local equilibrium, and one at overall equilibrium. Then, the resulting simulations are compared to an experimental reference case from another study [23] that was performed at slow crystallization rate (to avoid kinetics effects). The aim is to model the hydrate volume in the end of the crystallization, and final pressure far from equilibrium. Another objective is to adjust the classic thermodynamic parameters (usually Kihara parameters) in the case where the equilibrium pressure is not sufficient.

This paper is organized as follows: Section 2 explains further the theory involved. Section 3 details the modeling approach with the two thermodynamic frameworks utilized. Section 4 then presents the simulation results in some details. In addition, a parametric study is suggested. Finally, the conclusion and some future works are discussed.

2. Theory

2.1. Calculation of VLE equilibrium

2.1.1. Calculating the vapor phase density

The vapor phase density and fugacity coefficient are usually calculated using an equation of state ($f(P,V_m,T) = 0$). Among the numerous equations of state available, the Soave-Redlich-Kwong (SRK) [33] is known to be a good choice for density calculation for vaporized small hydrocarbon molecules [5]. This equation was used with the parameters from Danesh [5].

Since we consider a constant volume, the knowledge of the vapor phase density defines the mass (or number of mole) of the initial gas phase ($=PV/Z_{SRK}RT$).

2.1.2. Calculating gas solubility in water

The gas molecule solubility into the water phase can be expressed from the equality of the chemical potentials (or the fugacities) of each molecules in the two phases (liquid and vapor). Considering a hydrocarbon gas mixture, a standard γ^∞/ϕ approach is usual [28]. The γ^∞ account for the activity coefficient at infinite dilution (Henry's law approach, introducing Henry's constants), while ϕ is the fugacity coefficient (calculated using an equation of state). Since the vapor–liquid equilibrium takes into account the hydrocarbon molecules only, the water molecule in the vapor phase is neglected. This leads to the following equation:

$$f^V = f^{L_w} \leftrightarrow P\phi_i x_i^{L_w} = x_i^{L_w} K_{H,i,w}(T,P_w^\sigma)\exp\left(\frac{PV_{m,i}^{\infty,L_w}}{RT}\right) \tag{1}$$

where $K_{H,i,w}$ is the Henry's constant of molecule i in liquid water L_w, and $V_{m,i}^{\infty,L_w}$ the partial molar volume of the molecule i at infinite dillution. In the same manner as our previous work [14], an average value of $V_{m,i}^{\infty,L_w} = 32 cm^3 mol^{-1}$ was used [18], and the Henry's constant were calculated from an empirical equation [30].

2.2. Thermodynamic equilibrium of clathrate hydrates

Phase equilibria are described by the equality of chemical potentials, μ, in each phase. In the case of clathrate hydrates thermodynamic equilibrium, this is the equality of water in both liquid and hydrate phase:

$$\mu_w^H = \mu_w^L \tag{2}$$

Actually, clathrate hydrate equilibrium is usually described by the van der Waals and platteuw model [35]. This model is based on classic thermodynamics for the water liquid phase (Gibbs-Duhem equation), and on statistical thermodynamics for the hydrate phase, based on the following assumptions:

- Each cavity contain one guest molecule at best,
- the interaction between the guest molecule and the cavity (water molecules) can be described by a pair potential function of the pair gas-molecule,
- the cavities are perfectly spherical,
- The guest molecules do not deform cavities,
- There are no interactions between the guest molecules.