



## Full Length Article

# A new predictive thermodynamic framework for phase behavior of gas hydrate



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## ABSTRACT

This study presents a thermodynamic framework for predicting hydrate equilibrium pressure of gas species including methane, ethane, propane, nitrogen, carbon dioxide and hydrogen sulfide and their mixtures. For this purpose, Peng–Robinson–Stryjek–Vera equation of state (PRSV-EOS) along with modified Huron-Vidal (MHV1) mixing rule and UNIQUAC model were employed to calculate fugacity and activity coefficient of water in equilibrated fluid phases. To represent phase behavior of solid hydrate, a modified version of van der Waals and Platteeuw (vWd-P) model was utilized which accounts for guest interaction with water molecules beyond first shell of cavity and also asymmetry of encapsulated molecules and cage structure. In addition, dissolution of gas compounds in aqueous phase and subsequent non-ideality of water was taken into account. It was realized that both physical phenomena are of marked influence on the prediction accuracy.

In contrast to conventional modelling approaches which scarify some part of equilibrium data to regress some adjustable parameters, advantageously, our model does not require any pre-matching. It was observed that present framework gives accurate prediction for equilibrium pressure of hydrates of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S with overall average absolute percent deviation (AAPD) 3.2, 3.4, 3.7, 1.5, 2.8 and 1.3, respectively. Also, incipient pressure of hydrate formed by binary gas mixtures comprised of aforementioned single components could accurately be predicted by proposed approach, which is detailed in the manuscript. Overall, formation pressures predicted by proposed modelling approach are more accurate (or at least comparable) to outstanding models presented in the hydrate literature.

## 1. Introduction

Clathrate hydrate is a solid compound comprised of gas components trapped in the cavities formed by hydrogen bonding of water molecules [1]. Simply put, hydrate forms an absorbent-like media to trap guest molecules, such as methane, ethane and any other small gas species. This crystalline solid is snow-like, but is not ice [2]. Gas hydrate is most often formed at temperatures above the melting point of ice in industrial processes and is able to encapsulate vast amounts of gas molecules [3]. The hydrate stability is due to forming hydrogen bonds between the host molecules, i.e., water molecules, and interactions between the guest/host molecules in cavities [4]. Based on the relative size and shape of cavities, hydrate can have different crystalline structures, namely, sI, sII, sH and amorphous type [5]. Of these structures, only sI and sII are normally encountered in oil and gas production processes [6].

Hydrate formation is a common, unfortunate event in gas transmission and operation which results in blockage of pipelines at

temperatures and pressures above the water freezing point, i.e., largely above the expected state of ice formation [7]. Also, gas hydrate occurs in various facilities of upstream petroleum industry such as in well bores during gas injection at high pressure and wellhead valves because of decreasing temperature caused by the Joule-Thompson effect. In spite of bothersome facets, hydrate offers beneficial opportunities for underground storage of huge amount of natural gas within much lower volumes [8]. Additionally, as declared by most geologist, massive gas resources are buried as hydrate form in depth of ocean floors and permafrost. Recently, specialists are also making use of hydrate in gas separation process [9]. As one could deduce, clathrate hydrate is becoming an intriguing subject for scientists and engineers to an extent that Shahnazar and Hasan asserted at near future 3 papers per day will be published about hydrate [10]!

In industrial processes, hydrate normally forms as two types of equilibrium systems including hydrate-liquid water-vapor (H-L<sub>w</sub>-V) or hydrate-ice-vapor (H-I-V), where former is of more interest. Hence, thermodynamic modelling of gas hydrate practically deals with

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computing equilibrium state of these two systems. To this end, some researchers provided correlations and empirical charts to estimate formation condition of gas hydrate. However, as the first well-based thermodynamic study, van der Waals and Platteeuw (in short vWd-P) developed a mathematical expression for describing stability of hydrate clathration process by applying principles of statistical thermodynamic [11]. According to this theory, hydrate formation process goes through two steps: first, free water molecules develop hydrogen bonds together and construct empty cages which act as absorbent sites (this stage is completely hypothetical). Afterwards, each empty cavities will be occupied by at most one guest molecules, i.e., gas compounds [12]. That is to say, vWd-P's model describes cage occupation as a Langmuir-like absorption process in which the empty hydrate lattice and guest molecules act as absorbent and absorbate, respectively [13]. To obtain Langmuir constants, originally, vdW-P took Lennard-Jones cell potential to account for interaction between encapsulated guest species and water molecules at the cage periphery [12]. But, further studies demonstrated much more accuracy and performance of Kihara potential while predicting hydrate phase behavior that has been predominate perception till now [14]. Recently, Hsieh et al. applied square-well (SW) potential to calculate Langmuir adsorption constants [15]. Obviously, as widely accepted cell-potentials such as Kihara and Lennard-Jones roughly represent guest-water interaction, using SW is a real over simplification! In order to compensate poor performance of SW potential, Hsieh et al. introduced an empirical expression with six adjustable parameters into their formulation to include compression of guest free volume in cavity due to high pressure effect [15]. Later, Chin et al. extended work of Hsieh et al. for representing hydrate phase behavior in presence of electrolytes and inhibitors [16]. In another notable study, Lee and Holder correlated reference chemical potential of water with parameters of Kihara cell-potential function [17]. Apparently, their approach does not involve all physical aspects of hydrate formation.

In contrast to unanimous agreement on reliability of vdW-P's model (of course in modified forms), most controversies (as numerous publications imply) have been over representation of phase equilibrium of coexisting fluid phases, e.g., vapor or liquid water, which directly impacts on calculation of adsorption constants [14]. It partly stems from the fact that performance of vdW-P's model (for calculating fractional occupation of cavities) strongly depends on selection of a proper model for calculating fugacity of components in equilibrated phases.

To deal with equilibrium state of fluid phases, numerous attempts have been made to augment vWd-P's model with proper EOS and/or activity coefficient models. For example, Karamoddin and Varaminian employed SRK and VPT as simple cubic EOS along with CPA to model hydrate dissociation pressure of some refrigerant. To obtain best prediction, they regressed unknown binary interaction parameters of vdW mixing rule as well as Kihara potential parameters using equilibrium data of hydrate phase [18]. In another study, Haghtalab et al. Electrolyte Cubic Square-Well (eCSW) EOS, which is based on Helmholtz free energy, to obtain equilibrium condition of common hydrate forming compounds ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CO}_2$  and  $\text{N}_2$ ) [19]. In this way, they inevitably sacrificed some of equilibrium data for fitting binary parameters of eCSW EOS. Following work of Hsieh et al., as mentioned above, Khosravani et al. used a six parametric empirical expression to represent depression of cage volume due to excessive pressure. Also, PRSV was applied in their investigation to calculate fugacity of water in both vapor and condensed phases. In oppose to this work, they used a Margules type mixing rule in order to account for interaction of species at the expense of requiring two adjustable parameter for each specific interaction [20]. Certainly, by increasing number of regression parameters, the modelling approach tends to be rather a data fitting work unable to extrapolate equilibrium condition beyond fitting range. In a recently notable study, Meragawi et al. took experience of fitting parameters of Kihara potential function for improving prediction performance of PR and PC-SAFT to model hydrate phase behavior.

Surprisingly, they conclude with better prediction of PR together with strong sensitivity of matching parameters [21]. Regarding this brief literature survey, one would infer a rigorous model should rely mainly on incorporating physical facets of equilibrium condition while using least regression parameters.

In spite of enriched hydrate literature, there is still some unsolved difficulties. For instance, local composition model, primarily proposed for calculating activity coefficient, could not explicitly incorporate effect of high pressure on phase behavior of liquid phase [22]. On the other hand, as exploiting hydrate resource is the current subject of industrial research, software developers would devise modules for simulating hydrate formation/dissociation in underground reservoirs [23]. However, most commercial softwares work based on simple cubic EOS, i.e., PR or SRK [24]. Therefore, for accurate prediction of hydrate formation/dissociation conditions, one necessarily needs an approaches combining both simplicity and high pressure applicability of cubic EOS with local composition models to represent complexity of species interaction in condensed phases.

In spite of substantial works conducted for prediction of hydrate formation conditions, most of them have focused narrowly on one side of problem, in particular extending original assumptions of vdW-P model, examining a new EOS for calculation of Langmuir constants or handling non-ideality of aqueous phase caused by dissolution of guest species. On the other hand, with a glance on hydrate literature, one might face numerous modelling approach in which authors exclusively made attempt to extend accuracy and reliability of their method by taking some new assumptions or introducing a few adjustable parameters. Undoubtedly, reliability of such approaches strongly relies on equilibrium conditions (temperature and pressure) taken for fitting unknown parameters. For instance, as pointed out by Klauda and Sandler [25,26], fugacity approach proposed by Chen and Guo [27] appreciably deviates from some experimental data beyond the temperature interval taken for fitting its parameters. By an extensive literature survey, one could infer lack of a definite modelling framework to represent hydrate phase behavior in whole range of thermodynamic conditions. All current models give predictions for limited set of conditions, mainly due to possessing adjustable parameters which make those models strongly dependent on chosen guest species and P-T interval. In other words, most available models serve as a fitting program with limited ability for extrapolation beyond regression interval.

In present work, we have taken main physical aspects of hydrate equilibria into account to construct a vigor thermodynamic framework by incorporating following points:

- 1) Effect of asphericity (or asymmetry) of lattice and guest molecules on absorption process and subsequently on Langmuir constants,
- 2) Non-ideality associated with VLE equilibria due to high pressure conditions and association of water molecules, and
- 3) Dissolution of gaseous species in aqueous phase as well as non-ideality of water component.

With the best of our knowledge, it is first time that all foregoing facets are regarded simultaneously for prediction of hydrate phase behavior. To this end, Peng-Robinson-Stryjek-Vera (PRSV) Equation of State coupled with first order modified Huron-Vidal (MHV1) mixing rule (detailed thoroughly in following section) was utilized to handle phase behavior of fluid phases, which shall be regarded as another novelty of this work. Advantageously, the proposed framework does not need any primary fitting (correlation) of parameters and offers a straightforward prediction for equilibrium pressure of I-H-V and  $L_w$ -H-V systems. In remaining parts of the paper, a thorough description of modelling approach has been presented and performance of our thermodynamic framework has been evaluated via comparison with experimental data and prediction of other models.

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