De-escalating Parametric Structure of Gas Hydrate Phase Equilibrium

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Abstract

Gas hydrates find remarkable potential for application towards energy, water, transport and storage, making them a truly technological compound of the 21st century. The hydrates are generally occurred in a co-presence with vapor and liquid phases. Since each of these phases is in a state of constant interaction with the other, any variation in the composition of an individual phase leads to affect the three-phase equilibria. The van der Waals and Platteeuw (vdWP) theory provides an important foundation for the statistical characterization of the hydrate phase. In this work, we employ this theory to propose a thermodynamic framework that provides individual phase assessments and identifies suitable hydrate formers for applications to, such as, desalination and load management systems. However, like many conventional methodologies, the model exhibits high degree of linked parametricity. This linkage entails two crucial issues: highly correlated model parameters with the vapor-liquid equilibrium descriptors, and existence of multiple sets of parameters that represent the same set of binary interactions. This results in infinite sets of parameters for the hydrate-liquid-vapor equilibrium description based on vdWP theory, which further leads to a severely fractionated approach. When a new component is added to the system, this linked parametricity gets compounded further, severely limiting the applicability of this class of thermodynamic models. This work addresses the crucial issue of linked parametricity of the hydrate phase that persists for more than last 60 years based on insights from the thermo-physics of gas hydrates as well as *ab initio* and molecular dynamics simulations. In particular, we describe the hydrate phase as a solid solution and re-visualize its stability affected by interactions between species of different phases, formulate the set of non-covalent interactions contributing to lattice stability, and revise lattice crystallography to comprehensively describe the hydrate phase. Gaining the phenomenological insights, either individually or in combination, we successively alleviate the parametric dependencies of hydrates for single to multiple guests, pure to salts (single and multiple salts) water and sI to sII hydrates. This allows us to characterize the hydrate phase based only on fundamentally derived properties and sever its linkage with VLE descriptors. This work has applicability towards both fundamental understanding of hydrates and technology development.

Keywords: Gas hydrates, thermodynamic modeling, non-covalent interactions, parameter-free model, molecular simulations, salts, mixed guests