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Abstract

We have developed a new model for compressible clathrates that extends the well-known van der Waals and Platteeuw model. The new model is derived by dispensing with the assumption of constant cages radii in the partition function level, resulting in new thermodynamically consistent expressions relating thermodynamic properties of the hydrate phase and the empty lattice isochoric reference. One set of additional parameters to the clathrate modeling framework is introduced, consisting of a scaling factor for each cage radius relative to the edge length of the unit cell. No additional guest-dependent empirical parameters are required. The model exhibits two features not previously reported in the literature: (i) a pressure shift between the clathrate being described and the empty lattice isochoric reference, and (ii) differences in the edge length of the unit cell and in the cages radii for different guest species at the same temperature and pressure, as a consequence of the sorption of guests. We also propose a test for thermodynamic consistency at high pressure, based on the multicomponent and multiphase Clapeyron equation. Using this test, we show that the proposed model solves an inconsistency issue observed in phase equilibrium calculations with some of the compressible clathrate models currently in use. We have performed parameter optimization for methane, ethane, and xenon in sI hydrates. Two sets of results are presented: 3-phase equilibrium conditions; and lattice size versus temperature or pressure for each of these substances, along with available experimental data.

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