Development of thermodynamic modeling for high pressure equilibria containing hydrate

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In modeling hydrate phase, a classical Van der Waals and Platteeuw (VdWP) theory based on statistical thermodynamics is widely used. However, thermodynamic models for hydrate, a combination of equation of state and original VdWP theory, was found to be only applicable to low and medium pressure region since the lattice distortion effect is ignored in VdWP theory. We developed a thermodynamic model for hydrate prediction by following two steps; (1) A original VdWP theory is improved by formulating the lattice distortion effect into the theory. (2) A non-random lattice fluid with hydrogen bond (NLFHB) is corrected to accurately reproduce the PVT behavior of water up to 1000 MPa. By fitting the developed model to both dissociation pressure and the lattice parameters of pure and binary guest mixtures, for six components, we obtained new hydrate parameter sets including Kihara potential and empty hydrate vapor pressure equation. The calculation results showed that, at high pressure region, the developed model closely describes the experimental retrograde behavior of CH_4 and CO_2 in dissociation pressure and the correlated lattice parameters accurately agree with the experimental values.