Thermodynamic Evaluation of Gas Hydrate Phase Equilibrium Data with Additives

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Gas hydrates are a class of crystalline materials in which simple small gases are trapped inside a framework of hydrogen-bonded water molecules. The formation of hydrates in oil and gas production and transportation pipelines needs to be well managed due to the potential safety risk and economic loss required for recovery. Phase equilibrium of gas hydrates is vital in developing thermodynamic models to predict their phase behaviors and properties. While improving those prediction models essentially relies on the accuracy of the reported hydrate phase equilibrium data, a reliable evaluation of such accuracy has not been yet formulated. This presentation will present how we can evaluate the thermodynamic consistency of hydrate phase equilibrium data for systems with additives. The criteria for evaluation, including the consistency of the heat of hydrate dissociation (gas hydrate phase) and the water activity (liquid water phase), are obtained from fundamental thermodynamic principles. The quantitative evaluations of CH₄ hydrate systems (195-302 K and 1-186 MPa) in the presence of thermodynamic hydrate inhibitors such as methanol, glycols (monoethylene glycol, diethylene glycol, triethylene glycol, glycerol), salts (NaCl, KCl, MgCl₂, CaCl₂), and amino acids (glycine, L-alanine, L-serine, L-proline) are performed to verify the reliability and generality of this method. This presentation thus provides a guideline on the evaluation of the thermodynamic consistency of a guideline on the evaluation of the thermodynamic consistency of hydrate in terms of quantitative index.