Phase Equilibria with Hydrate Formation in H_2O + CO_2 Mixtures Modeled with Reference Equations of State

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Formation conditions of pure CO_2 gas-hydrates, i.e. clathrates, were predicted with a new hydrate phase model combined with the reference equations of state (EoS) for H_2O and CO_2. The hydrate model adapted from A.L. Ballard and E.D. Sloan [1] was modified for pure CO_2 hydrates in this study. Temperature and pressure dependences of the molar volume of the reference empty water lattice were determined from the experimental data for the lattice parameter of CO_2 hydrates. The Langmuir constant, describing the composition of the hydrate phase, was calculated from the Kihara cell potential function. The heat capacity of the empty water lattice was approximated using the IAPWS formulation for ice Ih [2]. The main advantage of this CO_2 hydrate model lies in the fact that it is based on the crystallographic data. The reference Gibbs energy and the reference enthalpy of the empty water lattice are the only quantities correlated to hydrate formation phase equilibrium *p-T* data. Properties of other phases, namely the water-rich liquid, carbon dioxide-rich liquid, vapor, water ice, and dry ice, were computed with reference EoSs, including the IAPWS 95 EoS for water by Wagner and Pruss [3], the reference EoS for CO_2 by R. Span and W. Wagner [4], the IAPWS EoS for H_2O ice Ih by R. Feistel and W. Wagner [2], and a new EoS for dry ice by A. Jäger and R. Span [5]. New mixing rules for the reference EoSs of the H_2O+CO_2 fluid phases [6] were employed in this study. Phase equilibria predicted by the new CO_2 hydrate model combined with the reference EoSs are in good agreement with experimental data for hydrate formation over wide temperature and pressure ranges.

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