

Extension of the van der Waals and Platteeuw Gas Hydrate Model for Hydrogen Hydrates

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In the transition to a carbon-neutral society, hydrogen is considered one of the most promising energy carriers. However, hydrogen transportation and storage remain challenges. Hydrate formation with hydrogen is either a risk to be avoided during transportation, or an opportunity for cheap, reversible, and environmentally friendly energy storage[1]. In previous works of our group, the most accurate multiparameter equations of state for thermodynamic properties of fluid phases have been combined with a gas hydrate model for CCS/U relevant mixtures[2–4]. Now, the gas hydrate model is extended for the description of pure hydrogen hydrates.

Small guest molecules, such as hydrogen, are known to occupy cavities in the water (host) lattice multiple times[5]. This phenomenon has significant impact on the stability of the hydrate phase and its thermodynamic properties. This study reviews available van der Waals and Platteeuw[6] based hydrate models considering multiple occupation of host cavities. The objective is to provide a comprehensive overview of the required correlations for the implementation of a computationally efficient *cluster* model that considers up to 5 guest molecules per cavity. Further, two methodologies for the estimation of molecular distances of hydrogen molecules inside the water cavities are introduced.

The model predictions for pure hydrogen hydrates are evaluated by comparison with available three-phase equilibrium data showing proper representation of the quadruple point and confirm the destabilization of the sII lattice at approx. 370 MPa. Fractional and total occupancies of the sII crystal structure are compared to results of other theoretical studies indicating that double occupancy of small sII cavities is improbable and 4-molecule occupation is predominant in large sII cavities for pressures above 300 MPa. The proposed model provides the framework for further exploration and optimization of energy solutions with hydrogen hydrates.

References

1. A. Gupta, G. V. Baron, P. Perreault, S. Lenaerts, R.-G. Ciocarlan, P. Cool, P. G.M. Mileo, S. Rogge, V. van Speybroeck, G. Watson, P. van der Voort, M. Houilleberghs, E. Breynaert, J. Martens, and J. F.M. Denayer, *Energy Storage Materials* **41** (2021).
2. A. Jäger, V. Vinš, R. Span, and J. Hrubý, *Fluid Phase Equilib.* **429** (2016).
3. S. Hielscher, V. Vinš, A. Jäger, J. Hrubý, C. Breilkopf, and R. Span, *Fluid Phase Equilib.* **459** (2018).
4. V. Vinš, A. Jäger, J. Hrubý, and R. Span, *Fluid Phase Equilib.* **435** (2017).
5. W. L. Mao, H.-K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, and Y. Zhao, *Science* **297**, 5590 (2002).
6. van der Waals, J. H. and J. C. Platteeuw, *Advances in Chemical Physics*, vol. 2, 1–57 (1958).