

## **Determination of Liquid Water + Hydrate + Carbon Dioxide Phase Equilibria by Use of Molecular Simulation**

Eric M. Grzelak

*Colorado School of Mines, Chemical & Biological Engineering Department, Golden, CO, U.S.A.*

David T. Wu

*Colorado School of Mines, Chemical & Biological Engineering Department / Chemistry Department, Golden, CO, U.S.A.*

Amadeu K. Sum<sup>C, S</sup>

*Colorado School of Mines, Chemical & Biological Engineering Department, Golden, CO, U.S.A.*

*asum@mines.edu*

As computational resources and techniques grow, more complicated systems are able to be studied. One area of computational research that is growing rapidly is the study of clathrate hydrates. These ice-like crystalline inclusion compounds provide both a potential energy resource and means of storing/transporting light gases. Many computational investigations have been published related to nucleation mechanisms, energy storage, and theoretical determinations of phase equilibria. However, only a few studies have rigorously considered the phase equilibria involving the models used. In this work we extend our knowledge of hydrate phase equilibria with the determination of liquid water + hydrate + carbon dioxide phase coexistence. This is done using the TIP4P/Ice model for water and both the EPM2 and TraPPE models for carbon dioxide. Techniques including thermodynamic integration, semi-grand canonical Monte Carlo and Gibbs ensemble Monte Carlo are employed to equate the free energies of each species in each phase. The results of our work are compared to both experimental values and computational results employing molecular dynamics techniques using the same models.