Thermodynamics and Kinetics Studies of the Formation and Decomposition of Clathrate Hydrates of Methane, Carbon Dioxide, and their Mixtures Using a Differential Heat Flux Calorimeter

G. Besnard, R.J. Martin*, and R. Kobayashi
Department of Chemical Engineering
Rice University
P.O. Box 1892
Houston, TX 77251 USA

A high pressure heat flux calorimeter in an isobaric temperature ramping mode has been used to measure the solubility. The solubility measurements emphasize a crystallization-like process taking place during hydrate formation prior to the appearance of any visible solids and hence, show a striking divergence from Henry's Law, the frequently used calculation procedure prior to and during hydrate formation. These measurements were further used to determine the enthalpies of solution dissociation and entropy changes. Moreover, the hydration numbers of these compounds provide some explanations and criteria of the stability of the cages of gas hydrates in the host lattice.

Finally, a kinetic study confirms the crystallization process of hydrate formation and exhibits a high level of ordering/supersaturation prior to hydrate formation including a substantial gas consumption rate during hydrate formation.

* Deceased, 1997