

## Methane+Ethane Hydrate Phase Equilibrium

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### ABSTRACT

Gases recovered from the hydrate stability zone in marine sediments and permafrost indicate that the methane/ethane ratio changes systematically with depth. Interpreting these results requires information about the stability of hydrates that form from water and gas mixtures. In particular, we need estimates for the partitioning of methane and ethane into hydrate and aqueous solution phases. We present phase equilibrium calculations for a system composed of methane, ethane, and water. The three components may be present in four possible phases: bulk gas, liquid, hydrate structure I, and hydrate structure II. Our calculations allow for the presence of both structure I and structure II because experimental results show that the two structures may coexist for mixtures of methane and ethane gases in water. The calculation of phase equilibrium may be viewed as an optimization problem. For a process at fixed pressure and temperature, the equilibrium state is defined by a global minimum in the Gibbs free energy  $G$ . We search for the minimum in  $G$  by adjusting the proportions of chemical components across all of the possible phases. Phases which are thermodynamically unstable disappear in the search for the global minimum in  $G$ .

Gibbs free energy is an extensive thermodynamic property, so it can be written in terms of chemical potentials. The chemical potentials of vapour and liquid mixtures are calculated using equation of state (e.g. Tebble and Bishnoi, 1988), while the chemical potentials of components in the hydrate phases are calculated using the solid solution model of van der Waals and Platteeuw (1959). The resulting estimate of  $G$  is a nonlinear function of pressure, temperature, and composition. The composition is defined by the number of moles of each component in each possible phase. For prescribed values of pressure and temperature,  $G$  depends solely on sets of the numbers of moles of the three components in the four possible phases. Conservation of the three components reduces the number of independent variables from 12 to 9. The additional constraints are imposed by the solid solution model for the two hydrate structures, so there are a total of 7 independent variables in the optimization problem. We solve the optimization problem using a simulated annealing algorithm. The variables are randomly perturbed to search for the global minimum in  $G$  at fixed values of pressure and temperature. This calculation is repeated using different values of pressure and temperature to map the phase diagram.

We calculate phase diagram for a methane-ethane-water mixture at 10 MPa when the initial ratio of methane to ethane is 90:10 and 99:1. In calculations with 10 % of ethane, there are two stable hydrate structures between temperature 0 C and 13 C. We also find a zone between 13 C and 16 C where hydrate structure II coexists with the aqueous solution and bulk gas phases. In calculations with 1 % ethane, only structure I is the stable form of hydrate. In both calculations, the methane/ethane ratio in aqueous solution (e.g. ratio between the equilibrium concentrations of dissolved gas) increases from the bottom to the top of the hydrate stability zone. In calculation with 10 % ethane, the methane/ethane ratio increases by about 8 times across the stability zone, while a 5-fold increase is found in calculations with 1 % ethane. The methane/ethane ratio in the hydrate phase is almost constant in both calculations. However, it changes by a factor of three across the three-phase equilibrium zone.