

Homework 2
Advanced Materials Thermodynamics
Due Monday September 4, 2023

Clathrate hydrates of natural gases are solid crystalline cage structures composed of water and gasses such as hydrogen, methane, and carbon dioxide. These materials first became of importance in the petrochemical industry since they form at low temperatures and under high pressures which occur in petroleum recovery in deep wells and in the sea or in the arctic. Clathrates of methane, for instance, can clog pipes and lead to explosions or loss of product. Later, it was realized that the bottom of the ocean contains enormous deposits of methane hydrates that are close to their equilibrium point, meaning that a small increase in the ocean temperature can release devastating amounts of methane gas which could end life on earth through rapid global warming. Prehistoric events of this type have been documented in the fossil and arctic ice record. Clathrates have also been seen as low-pressure storage vehicles for green hydrogen; as a tool for industrial gas separation; and to as a disposal tool to permanently store CO₂ in a solid form. For these reasons clathrates may be of great importance to the survival of human and other life-forms. Yi W-Z, Li X-S, Yu Y-S, Chen Z-Y *Hydrate phase equilibrium and dissociation enthalpies for tetrahydrothiophene and different gas systems* Fluid Phase Equil. **559** 113497 (2022) have recently reported on studies using tetrahydrothiophene (THT) to enhance the formation of clathrates of hydrogen, methane, and CO₂. They found that tetrahydrothiophene can drastically reduce the requisite pressure and raise the temperature for clathrate formation.

- a) Yi uses the Clausius-Clapeyron equation to model the desorption of gas from clathrates. Derive the C-C equation as was done in class. What are the assumptions involved in this derivation. Are these assumptions appropriate at high pressures and low temperatures? Why or why not.
- b) Equation (2) is like the Clausius-Clapeyron equation. Show the origin of equation (2). Z is the compressibility factor which has a value of 1 for an ideal gas, $Z = PV/RT$, where V is the molar volume. Does this modification of the C-C equation make equation (2) appropriate for the extremely high pressures and low temperatures where Clathrates hydrates form?
- c) Yi uses the Peng-Robinson equation to calculate Z . Explain what a cubic equation of state is and how the PR equation relates to the van der Waals equation. What does the van der Waals equation account for that the ideal gas equation can't account for. Why might it be difficult to obtain a clathrate hydrate with the ideal gas law?
- d) The vapor pressure of a solute in a solution follows either Raoult's ideal solution law, $p^{\text{vap}} = p^{\text{vap}}_{\text{pure}} x_i$ where x_i is the mole fraction which is close to 1 for Raoult's law, or Henry's law for dilute solutions $p^{\text{vap}} = k_i x_i$ where k_i is the Henry's law constant. Equation (4) looks like the Clausius-Clapeyron equation. Derive equation (4) using the C-C equation derivation.
- e) Derive equation (3).