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Phase Equilibrium for Methane Hydrate from 190 to 262 K

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This work presents measurements on methane hydrate phase equilibrium in the three-phase region (ice + hydrate + vapor). Our results complement partial data sets from other laboratories and provide new results in the region 193–260 K. These data indicated that methane hydrate of structure I does not undergo a phase transition to structure II as proposed in recent literature.

Introduction

Many natural gas components can form clathrates (called gas hydrates) with water. In these compounds water molecules form almost spherical, cagelike structures around guest gas molecules. Assembly of these cages form a hydrate unit crystal. A review of these compounds has recently been given (*1*).

Gas hydrates may be distinguished by their crystal structures. The commonly occurring structures are structures I, II, and H, composed of different types of cavities. Structure I hydrate is composed of two types of cavities: two pentagonal dodecahedra having twelve pentagonal faces (5^{12}), and six $5^{12}6^{2}$ cavities having twelve pentagonal and two hexagonal faces. The structure II hydrate unit cell is composed of sixteen 5^{12} and eight $5^{12}6^{4}$ cavities, while the Structure H unit cell is composed of two $4^{3}5^{6}6^{3}$, three 5^{12}, and one $5^{12}6^{8}$ cavities.

The structures are also distinguished by the sizes of the gas molecules encaged in the cavities of different sizes. To date at most one guest molecule has been found to occupy any cavity. Structure I may enclathrate molecules ranging in size from methane (4.36-Å effective diameter) to trimethylene oxide (6.1 Å). Structure II may enclathrate molecules ranging in size from argon (3.8 Å) to isobutane (6.5 Å). Structure H may enclathrate guests of sizes from that of argon (3.8 Å) to methylcyclohexane (8.6 Å).

The van der Waals and Platteeuw (*2*) statistical thermodynamics model is most frequently used in fitting and in predicting the equilibrium conditions of hydrate formation. A recent use of the model by Lundgaard and Mollerup (*3*) suggested an unusual prediction of the phase diagrams of methane hydrates, obtained via minimization of the Gibbs free energy of the system. One of the predictions of Lundgaard and Mollerup was that a slight mismeasurement of the unit crystal cubic side (by as little as 0.02 Å in 12 Å) could cause a structural transition (I to II) on the three-phase (I–H–V) hydrate equilibrium line at a temperature of 170 K.

Such a transition would not be unique because cyclopropane and trimethylene oxide have the ability to form either structure I or II hydrates, depending on thermodynamic conditions. The simple hydrates of cyclopropane were shown to undergo structural transition in the temperature range of 257.1–274.6 K on the basis of data by Hafemann and Miller (*4*) and Majid et al. (*5*). Hydrates of trimethylene oxide undergo phase transition between 252.4 and 260.1 K as determined by Hawkins and Davidson (*6*).

Several other works (e.g., Holder and Hand (*7*), Adisasmito and Sloan (*8*), etc.) provided experimental evidence for structure I–structure II transition for hydrates of natural gas mixtures at temperatures above the ice point. However, for gas mixtures, the phase transition occurs as a principal function of gas composition.

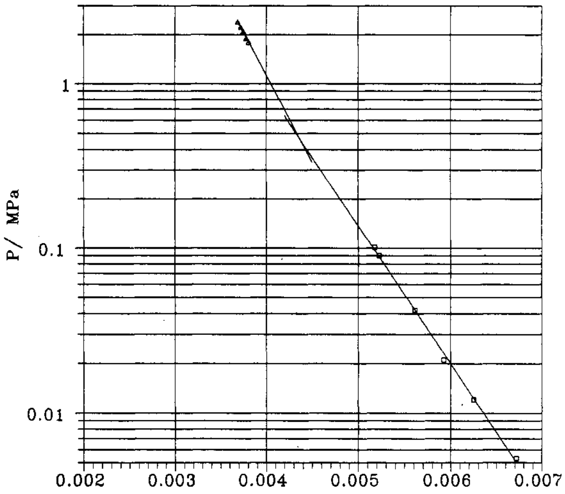

Figure 1. Methane hydrate equilibrium data: Δ, Deaton and Frost (*9*); □, Falabella (*11*).

For a single guest component hydrate, a solid-phase transition was indicated by a sharp change of slope in the three-phase pressure–temperature equilibrium line (discontinuity in $d(\ln P)/d(1/T)$). This slope change was due to the change in the enthalpy of hydrate formation, $\Delta_d H$, determined by the Clausius–Clapeyron equation applied to a univariant system.

The univariant Clausius–Clapeyron equation is given in eq 1 where P and T are the absolute pressure and temperature of hydrate equilibrium with vapor and ice, $\Delta_d H$ is the enthalpy of dissociation of hydrates, Z is the compressibility of the gas, and R is the universal gas constant. If $\Delta_d H/Z$ were constant

$$\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta_d H}{ZR} \tag{1}$$

over the temperature range, a plot of ln P against $1/T$ would be linear within a single structure. On the other hand, a nonlinear plot might indicate either a hydrate crystal structure change or a variable $\Delta_d H/Z$.

Experimental equilibrium data for methane hydrate formation below the ice point were available from multiple sources: Deaton and Frost (*9*) at 273–262.4 K, Roberts et al. (*10*) at 259.1 K, and Falabella (*11*) at 148.8–193.2 K. However, these data sets did not cover the temperature range 193–259 K. Linear fits for the available semilogarithmic data sets at temperatures above and below 210 K are shown in Figure 1. Fitted lines intersect at an angle which suggested a transition between structures I and II. The paucity of measurements

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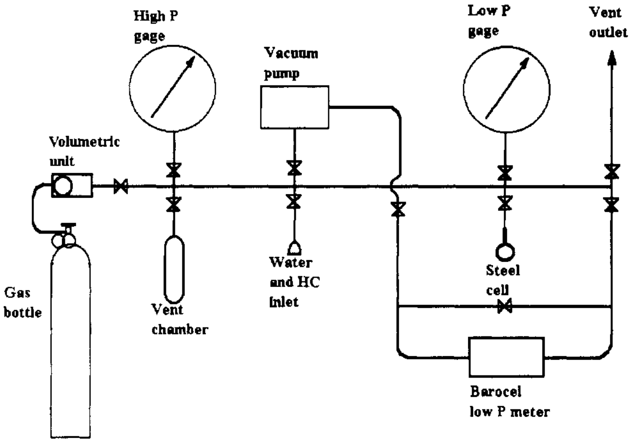

Figure 2. Apparatus design.

in the temperature range of 193–259 K suggested the experimental investigation of whether this transition might occur.

Experimental Equipment and Procedure

A schematic of the experimental equipment is given in Figure 2. The apparatus was built around a stainless steel spherical cell of 5.08-cm internal diameter rated for 10.1 MPa. The cell was filled with 150 stainless steel balls of 0.31-cm diameter, needed for surface renewal. A Thermolyne orbital shaker with 0.4-cm amplitude was used to agitate the stainless steel balls inside the cell a 16.7 rps. A cylinder of 99.9% pure methane from Matheson Inc. was used as a gas supply without further purification. The volumetric unit and the vent chamber shown on the diagram were not used in this set of experiments. Pressure was monitored via Heise gauges rated at 13.43 and 2.01 MPa. A Barocel differential electronic manometer (0.267-MPa full scale, 0.133-Pa resolution) was used at low pressures. A grease-sealed glass flask attached to the water and hydrocarbon inlet was used to vacuum distill water into the steel cell.

The cell was immersed in an 8L Neslab ethanol stirred bath. The bath was cooled using the Neslab cryocool CC-100 II two-stage immersion cooler. The minimal attainable temperature was 180 K. The operating temperature was maintained wtih the Neslab temperature controller with ±0.3 K stability and a 600-W immersion heater. Temperatures were measured with an Omega platinum resistance thermometer with ±0.1 K accuracy. The shaker frequency was selected to provide maximum cell agitation without excessive vibration.

The lines and cell were evacuated to 1 Pa. Water (degassed, deionized) was vacuum distilled into the cell partially immersed in liquid N_2. After the vacuum distillation process was complete, lines were reevacuated. The bath was set to a constant experimental temperature.

Figure 3 presents a schematic of the experimental procedure. The gas was admitted into the system, and 8–10 min was allowed for pressure and thermal equilibrium without agitating the cell. After the system had stabilized, the shaker was started and the presence drop was monitored as hydrates formed. When the pressure approached a near-equilibrium value (in several hours), some gas was vented from the system to decrease the system pressure below the expected equilibrium value. The hydrates which had previously formed dissociated, causing the pressure to increase and to approach the equilibrium value. After pressure stabilization at some new level, the system pressure was increased again. This process was repeated in successive approximations until the gap reached 1–2% of the absolute pressure, as shown on the right in Figure 3. The arithmetic average of the upper and lower pressure approximations was taken as the equilibrium value.

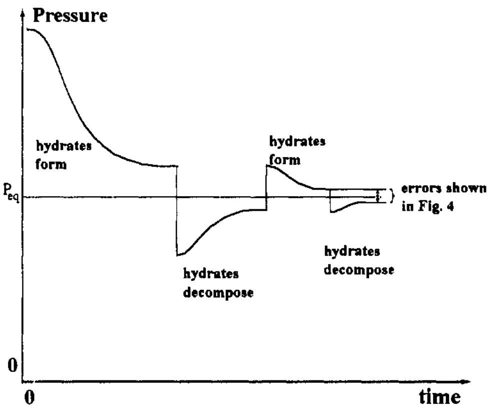

Figure 3. Experimental procedure schematic.

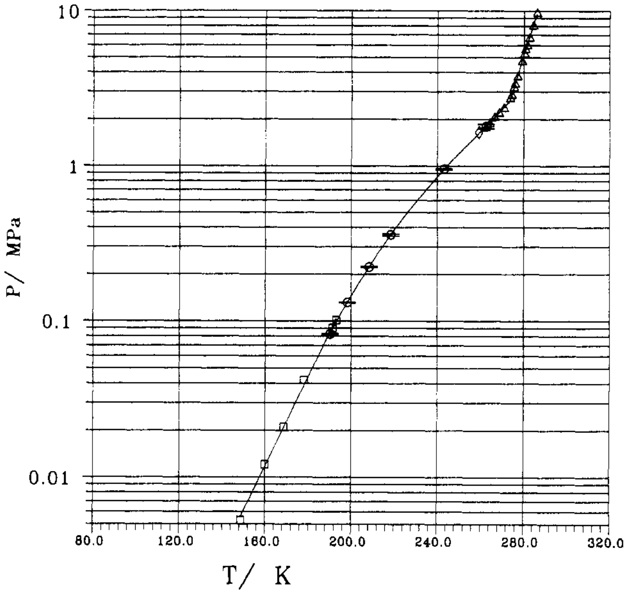

Figure 4. Methane hydrate equilibrium data: Δ, Deaton and Frost (*9*); □, Falabella (*11*); ◇, Roberts et al. (*10*); ⊙, this work. Only uncertainties in pressure were shown.

Table 1. Methane Hydrate Equilibrium Data

T/K	*P*/MPa	*T*/K	*P*/MPa
190.15	0.08251	218.15	0.3571
198.15	0.1314	243.15	0.9550
208.15	0.2219	262.40	1.798

Results and Discussion

The new equilibrium measurements are presented in Table 1 and in Figure 4 along with those of previous researchers. The two extremes of our measurements (at 262.4 and 190.15 K) fit smoothly with previous results of Falabella (*11*) and Deaton and Frost (*9*), respectively. This agreement suggested the validity of the apparatus and experimental procedure. The other values fit smoothly into the temperature gap, as complements to existing data. The reproducibility of our measurements was also determined by duplicate runs at 243, 208, 198, and 190 K, with the largest variation of 2.5% at 198 K.

We used the Clausius–Clapeyron equation and the hydrate heat capacity by Handa (*12*) in order to show that a smooth equilibrium line is expected with the absence of a phase transition in the region. Justification for use of this equation for univariant systems over a narrow temperature range comes from the fact that $\Delta_d H$ and Z do not change rapidly with temperature. Equation 1 can be used to determine the enthalpy of dissociation of the hydrate systems, as validated by Handa (*12*). This equation shows that the slope of the logarithm of the hydrate equilibrium pressure versus inverse equilibrium temperature is proportional to $\Delta_d H$. When a plot of $\Delta_d H$ against T is monotonic and continuous, then a plot of ln P against $1/T$ will have no slope discontinuity. It is also known that ΔH depends on T as follows:

$$\Delta_d H(T) = \Delta_d H(T_0) + \int_{T_0}^{T} \Delta C_p dT \qquad (2)$$

From this dependence it is seen that if a plot of ΔC_p against T is smooth, then so is $\Delta_d H$ against T in the absence of a phase transition. ΔC_p was evaluated using the stoichiometric formula

$$\Delta C_p = C_p(hyd) - 6C_p(\text{ice}) - C_p(\text{gas}) \qquad (3)$$

assuming that the unit cell of sI hydrate crystal is formed by six ice molecules and one gas molecule at total occupation of cavities by guest molecules. C_p(hyd) values were taken from Handa (*12*) and C_p(ice) and C_p(gas) were extrapolated from literature values (*13*, *14*) available for the region 23–271 K. Since both heat capacities of ice and methane do not deviate substantially from straight lines over the temperature region of interest, the conclusion may be drawn that $\Delta_d H$ and consequently the slope of ln P against $1/T$ should be continuous. This fact may be supported by the experimental evidence from the work of Majid et al. (*3*) for cyclopropane hydrates, where the sharp changes of slope of the hydrate equilibrium line were observed in the hydrate structural transition region.

The absence of slope discontinuities in the entire methane hydrate equilibrium line suggested that there was no structural transition of the structure I hydrates to structure II in the region of interest.

Conclusions

Equilibrium measurements on methane–ice hydrates are presented in the region 190–262 K. These results are consistent with existing values both above and below our temperature range. No structural transition is indicated.

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