Formation, Dissociation and Equilibrium of Argon Clathrate Hydrate at Temperatures below Water Freezing Point

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Abstract: This paper reports three-phase (ice + hydrate + vapor) equilibrium temperature-pressure conditions in the argon clathrate hydrate forming system at temperatures below the freezing point of water. The thermodynamic model of air clathrate hydrate at temperatures below freezing point of water is required for the analysis of the past climate change using the ice core from the ice sheets at Antarctica and Greenland because the formation of air clathrate hydrate affect the gas composition of air bubbles. The precise phase equilibrium conditions in argon clathrate hydrate forming system should be took into account for the thermodynamic model of air hydrate. The equilibrium conditions were measured by the batch, isochoric procedure. The measured temperature range is from 197.6 K to 241.7 K and the corresponding equilibrium pressure range is from 0.825 MPa to 3.723 MPa. The internal consistency of the measured equilibrium data are investigated by applying the Clausius-Clapeyron equation.

Key words: Clathrate hydrate, phase equilibrium, argon, ice sheet.

1. Introduction

There is a huge block of ice called ice sheets in Antarctica and Greenland. The ice sheets consist of many ice layers formed from compressed snow due to its own weight. Because the ice cores which are drilled from ice sheets contain the ancient air over the past 650.000 years, ice core researches for the analyses of the past climate change have been conducted on a long time.

The air trapped in the ice sheets exists as air bubbles in the shallow part of the ice sheets [1]. The bubbles react with surrounding ice and form the air clathrate hydrates at a certain depth of the ice sheets due to the overburden pressure [2], [3]. Clathrate hydrate, hydrate is ice-like compound composed of host water molecules and guest molecules. Every hydrate is stable at temperatures lower than the equilibrium temperature at a given pressure, or at pressures higher than the equilibrium pressure at a given temperature. The phase equilibrium condition of air hydrate is an indispensable physical property for analysis of air hydrate formed in the ice sheets. In the previous studies, the phase equilibrium condition measurements in the air hydrate forming system have been reported [4]-[6]. However, the composition of air in the ice sheets is different for each air bubble. In general, hydrates formed of a mixed gas like air have the guest molecules selectivity. It has been confirmed that in ice sheets oxygen is concentrated in hydrate and nitrogen is concentrated in air bubbles [7]. An important point for the analyses of the past climate change is how the

formation of air hydrates affect the gas composition of air bubbles and whether a correction is possible or not. A quantitative prediction how the gas composition will change due to the formation of air hydrates is necessary for gas analysis. Therefore, the thermodynamic model of air hydrate at temperatures below freezing point of water is required.

To construct the thermodynamic model of air hydrate, it is necessary to measure the phase equilibrium condition of the hydrate formed of each component of the air at temperatures below freezing point of water. Yasuda *et al*. [6] reported the phase equilibrium condition in the nitrogen and the modelled air hydrate forming systems at temperatures below freezing point of water. The mole ratio of the modelled air composed of nitrogen and oxygen is 0.790:0.210. In the previous studies, only nitrogen and oxygen were investigated and other components such as argon have been not taken into account. Nevertheless, phase equilibrium condition in the mixed gas hydrate forming system is more significantly influenced by component having the higher equilibrium temperature and the lower equilibrium pressure in the mixed gas components, even if its component is small amount. Argon hydrate has the higher equilibrium temperature and the lower equilibrium pressure than nitrogen and oxygen hydrates. There is a possibility that argon in the air affects the phase equilibrium condition of air hydrate significantly. It is necessary to confirm the influence of argon on the air hydrate by phase equilibrium condition measurements in argon hydrate forming systems at temperatures below freezing point of water

Phase equilibrium measurements at temperatures below freezing point of water are challenging because it is difficult to control the temperature and to operate vessel withstood low temperature and high pressure. The phase equilibrium measurements reported in the literature are limited in temperature range [5]. In this study, three-phase (ice + vapor + hydrate) equilibrium conditions in argon + water system were measured between temperatures 200 K and 240 K, using the isochoric procedure.

2. Experimental

2.1. Materials

We used deionized and distilled water (electrical conductivity was less than 0.5×10^{-4} S/m) and argon (99.999vol% certified purity, Japan Fine Products Co. Ltd., Kawasaki, Japan) without further purification.

2.2. Apparatus
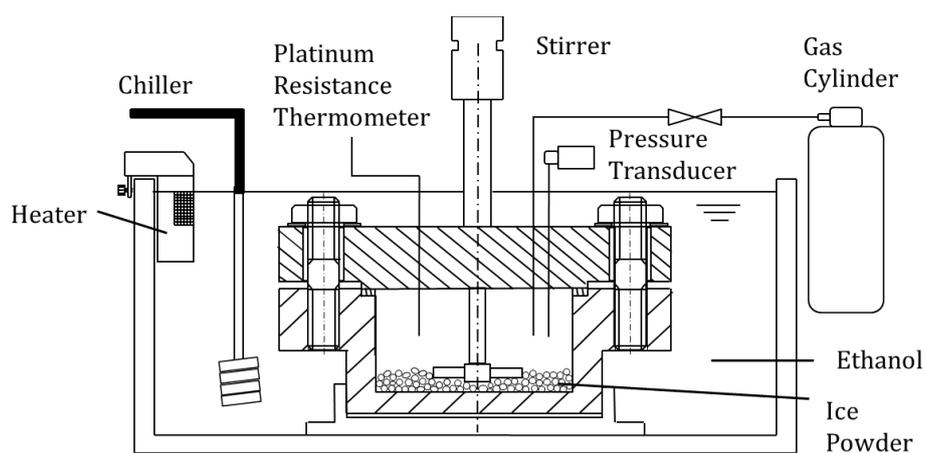
Fig. 1. Schematic of the experimental apparatus.

The overall configuration of experimental apparatus is shown in Fig. 1. The apparatus used in this study was the same as that was previously used for the phase equilibrium condition measurements below the water freezing temperature and the reliability was confirmed [8], [9]. The stainless steel vessel is immersed in a

temperature controlled bath. The bath was full of ethanol (99.5vol% certified purity). The inner volume of the vessel was 50 cm³ and a stainless steel gasket was used to seal the vessel. The inner pressure and temperature were measured by a strain-gauge pressure transducer (model PG-50KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan) and platinum resistance thermometer (Pt-100 Class B, Ichimura Metal Co., Ltd., Tokyo, Japan), respectively. The estimated uncertainty of pressure and temperature measurements with 95% coverage was ± 20 kPa and ± 0.3 K. A magnetic stirrer was used to agitate the fluid, ice and hydrate powder inside the vessel.

2.3. Procedure

The isochoric procedure was used to measure the equilibrium conditions. Before the measurements, approximately 8 g of ice powder which smaller than 1 mm was supplied into the cooled vessel. The experimental run was begun with removal of the air in the vessel by vacuum pump and pressurization with argon gas. Initial pressure-temperature condition was set free from hydrate formation in each experimental run. After lowering the temperature, sharp pressure drop was observed due to formation of hydrate. The temperature was maintained constant for 120 h to form the sufficient amount of hydrate. First the temperature was gradually increased in steps of 1.0 K. After the sudden pressure increase was observed due to dissociation of hydrate, the temperature was carefully increased in steps of 0.2 K. At every temperature step, the temperature was maintained constant for 24 h to achieve a steady equilibrium state in the vessel. After the complete dissociation of hydrate, slight pressure increase was observed because the pressure increase was only due to the thermal expansion of vapor. In this way, a pressure-temperature diagram was obtained for each experimental run and the point at which the slope of pressure-temperature diagram sharply changes was considered to be the three-phase equilibrium condition.

3. Results and Discussion
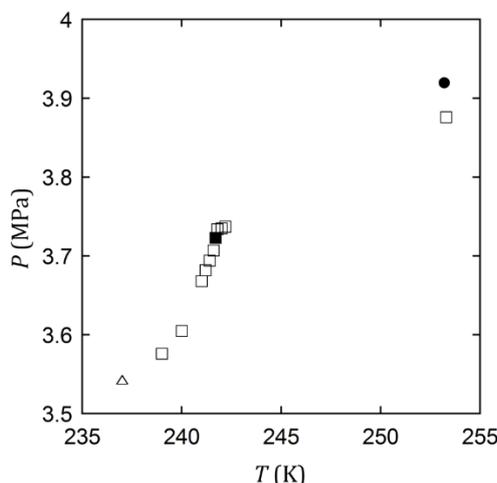
Fig. 2. Sequential pressure-temperature data during the representative measurements for three-phase (ice + vapor + hydrate) equilibrium conditions in argon hydrate forming system. ●, initial; △ argon hydrate formation; □, stepwise temperature increasing process; ■, obtained phase equilibrium conditions.

The representative pressure-temperature diagram obtained during an experimental run is shown in Fig. 2. The initial condition was set at 253.2 K, 3.920 MPa (circle plot in Fig. 2). Then, the temperature was decreased to 237 K (triangle plot) to form argon hydrate. After keeping 237 K for 120 h, the temperature was increased stepwise (square plots). The slope of pressure-temperature diagram sharply changes at 241.7 K, 3.723 MPa (black square plot), which corresponds to the complete dissociation of the hydrate. This point was

determined to be the three-phase equilibrium condition of argon hydrate. At the end of the measurements, the pressure did not recover to the initial level, while the temperature was increased to 253.3 K that is the same as the initial temperature within the uncertainty. The difference between the initial and recovered pressure was 44 kPa in this run. This deficiency of the recovered pressure to the initial pressure was ascribed to the hydrate remaining in the ice particles. This phenomenon is the so-called anomalous preservation effect [10], [11].
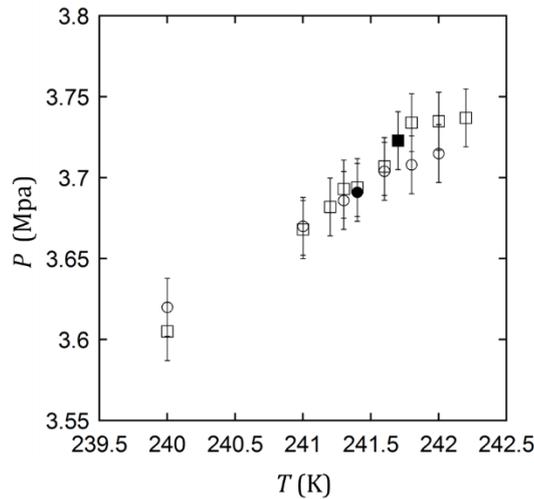
Fig. 3. Sequential pressure-temperature data obtained from replicate experiments for three-phase (ice + vapor + hydrate) equilibrium conditions in argon hydrate forming system.
(□, ○), heating process; (■, ●), obtained equilibrium conditions.
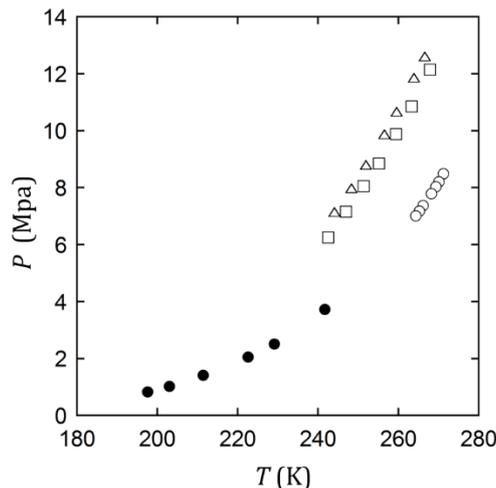
Fig. 4. Three-phase (ice + vapor + hydrate) equilibrium conditions in argon, nitrogen and air hydrate forming system. ●, argon hydrate (This study) ; ○, argon hydrate (Mohammadi and Richon) [5] ; △, nitrogen hydrate (Yasuda and Ohmura) [6] ; □, air hydrate (Yasuda and Ohmura) [6].

We performed replicate experiment with the same initial condition. The initial pressure, temperature and mass of ice particles are 3.92 MPa at 253.2 K with 6.603 g of ice for the first run and 3.906 MPa at 253.2 K with 6.610 g of ice for the second run. The sequential pressure-temperature data during the measurements are shown in Fig. 4. The three phase equilibrium pressures were measured 3.723 MPa at 241.7 K for the first run and 3.691 MPa at 241.4 K for the second run (black plots). The system pressure recovered to 3.876 MPa for the first run and to 3.853 MPa for the second run. The system pressures did not recover to the initial level

in both of the runs due to the anomalous preservation effect [10], [11]. The difference between the recovered pressures was accounted for the difference of the amount of hydrate remaining in the ice particles between the first and second runs. The system pressures at 241.3 K and 241.4 K obtained during the both of runs were mutually consistent within the uncertainty of the pressure measurements, as shown in Fig. 4. This consistency supports the reproducibility of the measured phase equilibrium conditions in the present study.

Table 1. Three-Phase (Ice + Vapor + Hydrate) Equilibrium Conditions in Argon Hydrate Forming System[a]

T (K)	P (MPa)
197.6	0.825
203.0	1.024
211.4	1.410
222.6	2.056
229.1	2.509
241.7	3.723

[a] Expanded uncertainties ($k = 2$) U are $U(T) = 0.3$ K and $U(P) = 20$ kPa.

Table 1 shows the three-phase (ice + hydrate + vapor) equilibrium temperature-pressure conditions in the argon hydrate forming system measured in the present study. The measured temperature range is from 197.6 K to 241.7 K and the corresponding equilibrium pressure range is from 0.825 MPa to 3.723 MPa. The plotted data is shown in Fig. 3 with the equilibrium data in argon hydrate forming system reported by Mohammadi and Richon [5] and the equilibrium data in nitrogen and modelled air hydrate forming system reported by Yasuda et al [6]. The equilibrium pressure increases with an increase in temperature. The measured equilibrium data are aligned on a single smooth curve as shown in Fig. 3. This alignment supports an internal consistency and the reliability of the measured equilibrium data. The equilibrium pressure in argon hydrate forming system is lower than that in nitrogen and air hydrate forming system at given temperature, as shown in Fig. 3.
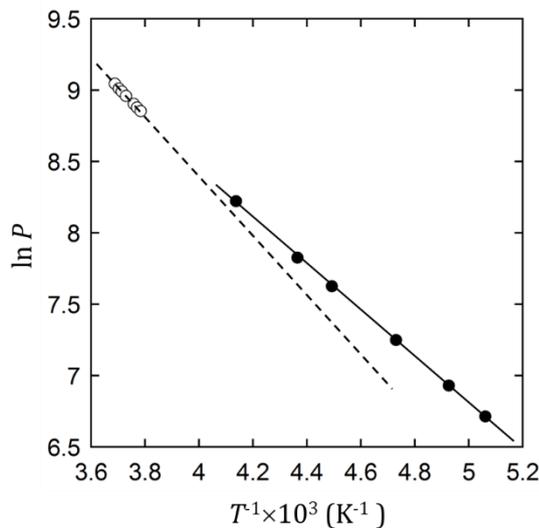
Fig. 5. Three-phase (ice + vapor + hydrate) equilibrium conditions in argon hydrate forming system, plotted on lnP versus T⁻1 plane. Solid line: a liner correlation of the equilibrium data measured in this study. Dashed line: a liner correlation of the equilibrium data measured in the literature [5]. ●: This study. ○: Mohammadi and Richon [5].

The equilibrium data are plotted on an $\ln P$-T^{-1} plane, as shown Fig. 5, to consider the internal consistency of the measured equilibrium condition data and to compare the measured equilibrium data with the

literature data. The measured data are aligned along a straight line. The liner correlation is also shown in Fig. 5. According to Clausius-Clapeyron equation, these slopes are expressed as follows:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T^{-1}} = -\frac{\Delta h}{zR} \tag{1}$$

where Δh is the enthalpy of hydrate formation/dissociation based on molar guest gas, z is the compressibility factor of the gas and R is universal gas constant. The compressibility factors z of argon gas are from 0.95 to 0.97 under the measured equilibrium conditions [12]. The straight correlation line indicated that the formation/dissociation enthalpy and compressibility factor are constant at equilibrium conditions, based on the Clausius-Clapeyron equation. The constant formation/dissociation enthalpy indicates that the crystal structure of hydrate does not change. This good agreement between the measured data and the correlation line supports the internal consistency of the present study. However, Fig. 5 shows different slopes of correlation line between the measured equilibrium data and the literature data. It is favorable to measure the phase equilibrium conditions in argon hydrate forming system at the covering range of temperatures in the literature [5].

4. Conclusion

The three-phase (ice + hydrate + vapor) equilibrium temperature-pressure conditions in the argon hydrate forming system were measured at temperatures below the freezing point of water. The measured temperature range is from 197.6 K to 241.7 K and the corresponding equilibrium pressure range is from 0.825 MPa to 3.723 MPa. The internal consistency of the measured equilibrium data are investigated by applying the Clausius-Clapeyron equation. The measured data were compared with the previously reported values. To construct the thermodynamic model of air hydrate, it is favorable to further measure the phase equilibrium conditions in argon hydrate forming system.

Acknowledgment

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