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Phase equilibrium for argon clathrate hydrate at the temperatures from 197.6 K to 274.1 K

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ABSTRACT

The phase equilibrium conditions of clathrate hydrate of argon were measured by the isochoric procedure at the temperatures from 197.6 K to 274.1 K. Argon hydrate would have industrial applications including a working medium of the hydrate-based heat pump systems as well as influence the analysis of the past climate change on the Earth. Nevertheless, the equilibrium conditions of argon hydrate were limited in the literatures and not reported below the temperature 264 K. The lowest and the highest measured equilibrium pressure is the pressure 0.825 MPa at the temperature 197.6 K and the pressure 9.881 MPa at the temperature 274.1 K. The equilibrium pressure increases with an increase in temperature. The reliability of the measured equilibrium conditions is supported by the internal consistency of those and the coincidence of the experimentally determined quadruple point (vapor + hydrate + ice + aqueous phases in equilibrium) temperature with the water freezing temperature theoretically predicted. The discussion is given on the comparison of the equilibrium data measured in this study and those reported in the literature.

1. Introduction

Clathrate hydrate (hereafter abbreviated as hydrate) is an ice-like inclusion compound composed of “host” water molecules and other “guest” substances such as light hydrocarbons, carbon dioxide, nitrogen, and noble gases. Hydrate has several unique characteristics: high gas storage capacity (up to 160 times denser than gas at standard temperature and pressure), large heat of formation/dissociation (up to 1.5 times larger than that of ice per mass), guest selectivity (fractionation between gas and hydrate phases), and “self-preservation” phenomenon (anomalously slow dissociation below the water freezing temperature despite under thermodynamically unstable conditions). Technologies utilizing hydrate were widely proposed, e.g., ozone storage [1], solid carbonated food [2], heat pump/engine [3,4], thermal energy storage as phase change material [5], gas purification [6], and fire extinction [7]. The operation conditions and performance of those technologies are based on the thermophysical properties of hydrate [3]. The measurements of the thermophysical properties can lead to develop hydrate-based technologies previously proposed and to create noble technologies utilizing hydrate.

Hydrate is also occurring in nature [8–10]. An example of hydrate naturally occurs is air hydrate in ice sheets on Antarctica and Greenland [11,12]. Ancient atmosphere is trapped in ice sheets and is isolated from the contemporary atmosphere. The trapped air is a direct clue of the past climate change. Air bubbles change to air hydrate in the deep ice sheets because low temperature and high pressure in the deep ice sheets is appropriate to form hydrate [13]. Composition of air bubbles in ice sheets changes with hydrate formation due to fractionation of hydrate, that is, N_2/O_2 ratio of air bubbles increases with hydrate formation [14]. Air hydrate in ice cores cannot be neglected to reconstruct the ancient air from bubbles in ice cores.

Hydrate is thermodynamically stable at higher pressures than the phase equilibrium pressure at a given temperature, or at lower temperatures than the equilibrium temperature at a given pressure. Phase equilibrium conditions of air hydrate should be a basis for further understanding of the climate and environment on the Earth. The phase equilibrium conditions of nitrogen hydrate [15], oxygen hydrate [16], $N_2 + O_2$ hydrate (formed from $N_2 + O_2$ gas mixture) [15], and “Air” hydrate (composition was not specified) [16] were measured below the water freezing temperature. The critical size of nucleus and energy barrier for air hydrate were estimated based on the measured equilibrium conditions and hydrate forming conditions in ice sheets [17].

The influence of argon (approx. 0.9 mol% in dry contemporary atmosphere) on the phase equilibrium conditions of air hydrate has been neglected in the previous analysis due to the limitation of measured data. The phase equilibrium pressure of hydrate

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formed from gas mixture is generally lower than a weighted average pressure of simple hydrate (formed from simple guest) forming pressure [18]. The equilibrium conditions of air hydrate should not be estimated by weighted average of those of simple hydrate. In fact, the analysis of air hydrate based on the equilibrium conditions calculated by weighted average of the simple hydrates may lead inaccurate conclusion that some air hydrate exists in the ice sheets under unstable conditions because of "self-preservation" of hydrate [19]. An analysis based on the measured equilibrium conditions of $N_2 + O_2$ hydrate revealed that the air hydrate exists under thermodynamically stable conditions [17]. For further accurate geophysical analysis on the Earth, influence of argon on the phase equilibrium conditions of the air hydrate should be considered because the phase equilibrium pressure of argon hydrate is approximately half lower than that of nitrogen hydrate and oxygen hydrate. The composition of the air bubble gradually changes with formation of hydrate in ice sheets. Statistical-thermodynamics model proposed by van der Waals and Platteeuw (vdW-P model) [18] is a powerful tool to estimate the equilibrium conditions of hydrate at a given thermodynamic state: temperature, pressure, compositions and *etc*. In vdW-P model, the inter-molecular parameters for the equilibrium condition estimation are generally adjusted to give a good agreement between experimental and predicted equilibrium conditions [20,21]. The phase equilibrium condition measurements of argon hydrate will be useful to estimate the equilibrium conditions of air hydrate in ice sheets that formed from varied air composition and may lead to better understanding for the ice sheets physics. The equilibrium conditions of argon hydrate were limited in the literature and not reported below the temperature 264.3 K [22,23], whereas those of nitrogen hydrate and $N_2 + O_2$ hydrate were measured above the temperature 243 K [15]. In this study, the three-phase (argon-rich vapor + hydrate + ice/aqueous) equilibrium conditions were measured at the temperatures from 197.6 K to 274.1 K. The quadruple point (vapor + hydrate + ice + aqueous) was also determined experimentally.

Table 1
Specification of the materials used in this study.

Chemical name	Chemical formula	Supplier	Purity
Water	H_2O	Laboratory made	Electrical conductivity was less than 0.5×10^{-4} S/m
Argon	Ar	Japan Fine Products Co. Ltd.	0.99999 vol fraction was certified

2. Experimental

2.1. Materials

The materials utilized in the experiment are specified in Table 1 with their purities. The distilled water and argon gas were used. The distilled water was deionized prior to the distillation in our laboratory. The electrical conductivity of the distilled water was$<0.5 \times 10^{-4}$ S/m. The argon gas was supplied with 0.99999 vol fraction certificated purity and utilized without further purification in the laboratory.

2.2. Apparatus

Two pressure vessels were used in this study for the phase equilibrium condition measurements dependent on the experimental temperature. The schematic of the pressure vessels is shown in Fig. 1. The pressure vessel was sealed with a stainless-steel V-gasket for $T < 243$ K, whereas sealed with a nitrile rubber O-ring for $T > 243$ K. The reliability of the vessels was confirmed in the previous phase equilibrium condition measurements [15,24–27]. The phase equilibrium conditions were measured by the isochoric procedure through the formation and dissociation of hydrate in the closed pressure vessels [27]. The inner sizes of the vessels were 40 mm diameter and 40 mm height for $T < 243$ K, and 80 mm diameter and 40 mm height for $T > 243$ K. A magnetic stirrer was equipped to agitate the inner fluid, ice and hydrate crystals. The vessels were immersed in temperature-controlled bath filled with ethanol for $T < 243$ K or ethylene glycol aqueous solution for $T > 243$ K. The inner pressure of the vessels was measured by a strain-gauge pressure transducer (model PG-50KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan for $P <$ 5 MPa; model PG-100KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan for $P > 5$ MPa). The estimated uncertainties of the pressure measurements were 17 kPa for $P < 5$ MPa and 18 kPa for $P > 5$ MPa with $k = 2$, where k denotes the coverage factor. A platinum resistance thermometer (Pt-100 Class B, Ichimura Metal Co. Ltd., Tokyo, Japan) was equipped to measure the inner temperature of vapor with the calibration against a Pt-100 reference thermometer (with certificated standard uncertainty 0.03 K, model Rf-100, Electronic Temperature Instrument Ltd., Worthing, UK). The estimated uncertainty of the temperature measurements was 0.15 K with $k = 2$. The sequential pressure and temperature data were acquired by a data logger (model GL820, Graphtec Corporation, Yokohama, Japan).

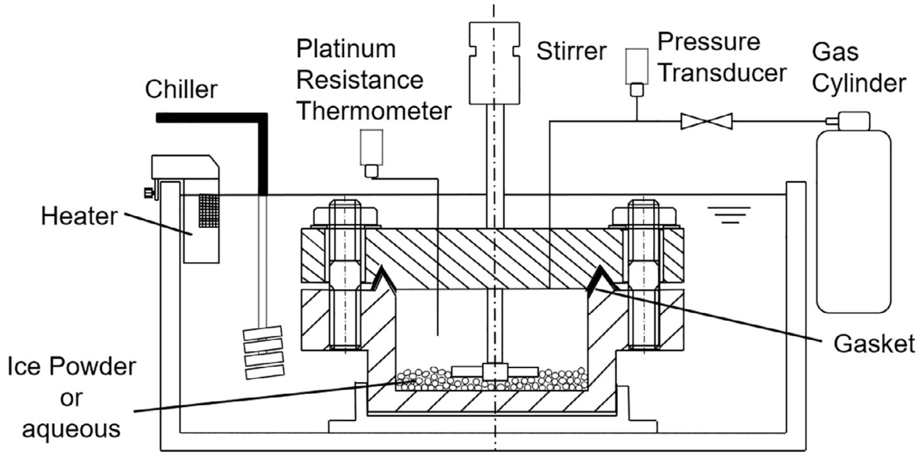

Fig. 1. Schematic of experimental apparatus. Stainless-steel V-gasket and nitrile rubber O-ring were equipped as gasket for $T < 243$ K and $T > 243$ K, respectively.