



# Phase equilibrium condition measurements in methane clathrate hydrate forming system from 197.3 K to 238.7 K



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## ABSTRACT

This paper reports three-phase (ice + vapor + clathrate hydrate) equilibrium conditions in methane + water system at temperatures between 197.3 K and 238.7 K. These equilibrium condition data could be applied for utilization of methane clathrate hydrate as a natural gas transportation medium, a working medium for heat pump/power generation cycles, and to further our understanding of the environments of planets and satellites. The equilibrium conditions were measured using the isochoric procedure. The measured equilibrium pressures are from 111.7 kPa at 197.3 K to 794.1 kPa at 238.7 K and increase with an increase in temperature. The internal consistency of the measured equilibrium data are examined by applying the Clausius-Clapeyron equation. Discussion is given on the comparison of the equilibrium data measured in this study to those reported in the literature.

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## 1. Introduction

Clathrate hydrates, or simply called hydrates, are crystalline inclusion compounds composed of host water molecules and other guest molecules, e.g. methane, carbon dioxide, nitrogen, oxygen and noble gases. Hydrates have several unique characteristics, e.g. large guest storage capacity, large heat of formation/dissociation, and guest selectivity. Due to these characteristics, hydrates could be industrially utilized as solid carbonated food [1], as a cool energy storage medium [2], and as a storage medium for ozone [3,4]. Hydrates naturally occur on Earth [5], as well as other planets and satellites in our Solar system [6,7]. Naturally occurring hydrates are an important aspect of planetary science because hydrates capture/release gaseous components from/into the atmosphere when formation/decomposition occurs; in some situations hydrates may become vast reservoirs of atmospheric gaseous and water. 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 pressure-temperature conditions of hydrates are the basis of the industrial utilization of hydrates and understanding the environments of planets and satellites.

Methane hydrates, hydrate containing methane, could potentially be utilized as a natural gas transportation medium [8] and as a working medium for heat pump/power generation cycles

[9,10]. Recently, the worldwide demand for natural gas has increased due to its lower CO<sub>2</sub> emissions with combustion, when compared to other fossil fuels, and the economic development of the developing countries. Currently, a significant amount of natural gas is transported as liquefied natural gas (LNG) because the density of LNG is approximately 600 times higher than that of gaseous natural gas. The extremely low temperature, approximately 111 K, required to liquefy natural gas means that the development of alternative natural gas transportation technologies is highly desirable. It has been suggested that natural gas could be transported in a gas hydrate form at a temperature of 253 K [8]. Due to this transportation temperature, natural gas hydrates have the potential to be a lower cost transportation medium for natural gas than LNG.

Hydrates may be also utilized as a working medium of heat pump/power generation cycles because hydrates have large amount of enthalpy change with their formation/decomposition [9,10]. Although theoretical performance analysis of hydrate based heat pumps has not been performed, analysis of a hydrate based power generation cycle, the reverse of the heat pump, has been performed [10]. The analysis revealed that operational conditions and performance of the power generation cycle depend on the phase equilibrium pressure and temperature conditions and the formation/dissociation enthalpy of the hydrate utilized. Furthermore, depending upon the guest gas used and the operational conditions, the guest gas was found to partially condense during the cycles. This condensation lowered the performance of the power generation cycle [10], and should therefore be avoided. Below the water freezing temperature, methane hydrate is a

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suitable candidate for a working medium because methane does not easily condense, owing to its low critical temperature, 190.56 K, and high vapor pressure, e.g. 4.5986 MPa at 190.56 K [11].

Methane hydrates may occur naturally on other planets and satellites in our Solar system, besides the Earth, e.g. Mars [7], Enceladus [6] and Titan [12,13]. On Mars, the existence of methane was detected by spectral observations, although methane in Mars has only short life time. The Cassini mission confirmed that rainfall on Titan is composed of liquid methane, while, on the surface, liquid methane lakes and rivers are commonplace [14]. The existence of extraterrestrial methane on these planets and satellites indicates the possibility of organic life and/or volcanic activity. However, the origin of methane in these cases has yet to be determined. It has been suggested that methane hydrate is a reservoir of methane and water on these planets and satellites [13]. Thus, the thermo-physical properties of methane hydrate is necessary to increase understanding of their climates and environments.

Although the phase equilibrium conditions of methane hydrate are important for the methane hydrate related engineering technologies and scientific issues, the measured equilibrium condition data are limited in the literature at temperatures below the water freezing point corresponding to the planets and satellites temperatures and industrial freezer temperatures. Furthermore, the literature data of the methane hydrate are scattering around temperatures 191 K and 244 K. Therefore, accurate measurements of the equilibrium conditions of methane hydrate are required. In this study, three-phase (ice + vapor + hydrate) equilibrium conditions in methane + water system were measured between temperatures 197.3 K and 238.7 K, using the isochoric procedure.

## 2. Experimental

### 2.1. Materials

The materials used in this study were deionized and distilled water and methane gas, as listed in Table 1. The deionized and distilled water was prepared using a laboratory water distiller (model WG 222, Yamato Scientific Co., Ltd., Tokyo, Japan). The electrical conductivity of the water used was less than  $0.5 \times 10^{-4}$  S/m. Methane gas was delivered by Takachiho Chemical Industrial Co., Ltd. (Tokyo, Japan) and used without further purification.

### 2.2. Apparatus

A schematic of the experimental apparatus used in this study is shown in Fig. 1. The apparatus used in this study was previously used for the phase equilibrium condition measurements below the water freezing temperature and the reliability of the apparatus was confirmed [15]. The main part of this apparatus is a stainless steel pressure vessel with an inner volume of 50 cm<sup>3</sup>. The formation and decomposition of methane hydrate in the isochoric procedure were performed inside the pressure vessel. A magnetic stirrer was used to agitate ice and hydrate powder and vapor inside the vessel. The pressure in the vessel was measured by a pressure transducer (with standard uncertainty  $\pm 0.8$  kPa obtained from test

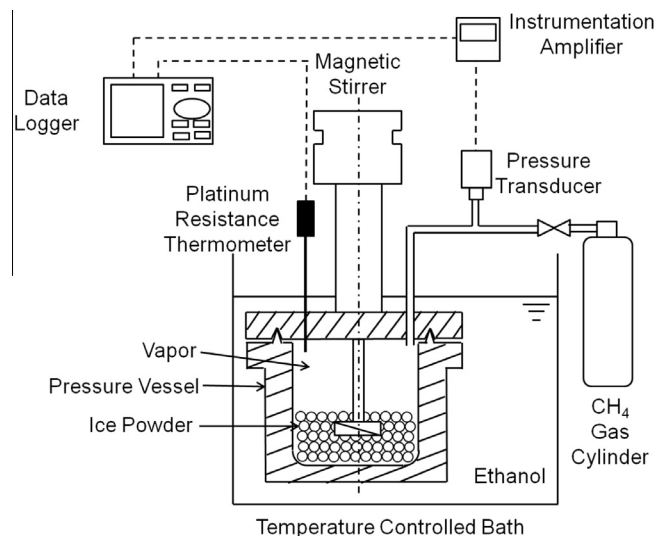


Fig. 1. Schematic of the experimental apparatus.

data sheet, model PG-10KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan) connected to an instrumentation amplifier (with certificated standard uncertainty  $\pm 0.4$  kPa, model WGA-670B, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan). The combined standard uncertainty of the pressure measurements was estimated to be  $\pm 0.9$  kPa from the uncertainties of the pressure transducer and the instrumentation amplifier. The temperature in the vessel was measured by a platinum resistance thermometer (Pt-100 Class B, Ichimura Metal Co., Ltd., Tokyo, Japan) calibrated against a Pt-100 reference thermometer (with certificated standard uncertainty  $\pm 0.03$  K, model RF-100, Electronic Temperature Instrument Ltd., Worthing, UK). The standard uncertainty of the calibration was determined to be  $\pm 0.07$  K. The combined standard uncertainty of the temperature measurements was estimated to be  $\pm 0.076$  K from the uncertainties of the reference thermometer and the calibration. The expanded uncertainties of the pressure and temperature measurements ( $k=2$ ) were estimated to be  $\pm 1.8$  kPa and  $\pm 0.15$  K, respectively. The pressure and temperature data were acquired by a data logger (model GL820, Graphtec Corporation, Yokohama, Japan). The temperature of the vessel was controlled by an ethanol filled temperature controlled bath (model TRL-080, Thomas Kagaku Co., Ltd., Tokyo, Japan).

### 2.3. Procedure

The isochoric procedure [16] was used to measure the three-phase equilibrium pressure and temperature conditions. The reliability of the procedure below the water freezing temperature was previously confirmed [17,18]. Equilibrium conditions were determined through the formation and decomposition of hydrate in the closed pressure vessel. A typical pressure-temperature diagram during the experimental run is shown in Fig. 2. Before the measurements, almost 7 g of fine grained ice powder, smaller than 1 mm, was supplied into the vessel. The mass of ice powder was measured by an electronic balance (model GF-3000, A & D Co., Ltd.) with the certificated expanded uncertainty of  $\pm 15$  mg ( $k=2$ ). The air inside the pressure vessel was discharged using a vacuum pump and methane gas was supplied to the vessel until the partial pressure of the air decreased to 0.1 Pa or lower. After the elimination of the air from the vessel, methane gas was supplied to the vessel at a prescribed initial pressure and the vessel was closed (square plot in Fig. 2). Then, the temperature of the vessel was decreased to form methane hydrate and then the pressure

Table 1  
Specification of the materials used in this study.

| Chemical name | Chemical formula | Supplier                                | Purity   |
|---------------|------------------|---|--|
| Water         | H <sub>2</sub> O | Laboratory made                         | Electrical conductivity was less than $0.5 \times 10^{-4}$ S/m |
| Methane       | CH <sub>4</sub>  | Takachiho Chemical Industrial Co., Ltd. | 0.9999 volume fraction was certified                           |

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