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Author(s)	Sugahara, Takeshi; Murayama, Shu; Hashimoto, Shunsuke et al.
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## **Fluid Phase Equilibria**

### **Paper**

## **Phase Equilibria for H<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O System Containing Gas Hydrates**

**Takeshi Sugahara, Shu Murayama, Shunsuke Hashimoto and Kazunari Ohgaki\***

Division of Chemical Engineering, Graduate School of Engineering Science,

Osaka University

Toyonaka, Osaka 560-8531, Japan

\*Corresponding author: Kazunari Ohgaki

E-mail: ohgaki@cheng.es.osaka-u.ac.jp

Fax: +81-6-6850-6290

### **Abstract**

Isothermal phase equilibrium (pressure - composition in the gas phase) for the ternary system of H<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O has been investigated in the presence of gas hydrate phase. Three - phase equilibrium pressure increases with the H<sub>2</sub> composition of gas phase. The Raman spectra suggest that H<sub>2</sub> is not enclathrated in the hydrate-cages and behaves only like the diluent gas toward the formation of CO<sub>2</sub> hydrate. This fact is also supported by the thermodynamic analysis using Soave - Redlich - Kwong equation of state.

**Keywords:** gas hydrate, solid-fluid equilibria, gas purification, Raman spectroscopy, hydrogen, carbon dioxide

## 1. Introduction

H<sub>2</sub> has attracted much attention as a clean and coming energy resource. The steam reforming of hydrocarbons is well known as the H<sub>2</sub> production processes. The gas generated by the steam reforming is a mixture composed of CO and CO<sub>2</sub> as well as H<sub>2</sub>. The Pressure Swing Adsorption (PSA) has been often used as one of the H<sub>2</sub> separation methods for such mixtures. A new H<sub>2</sub> separation process using the function of gas hydrates, instead of PSA having large-scale plants, is one of the potentialities because of its efficient storage and filling at high pressures. Gas hydrates are stabilized by the guest molecule enclathrated in the cage of water molecules and are classified into three types, structure-I, -II, and -H. These unit-cell structures are composed of two or three types of cages. All the structures have a common hydrate cage of pentagonal dodecahedron (5<sup>12</sup>, S-cage). In addition, the structure-I and structure-II have one other type of cage (5<sup>12</sup>6<sup>2</sup>(M-cage) or 5<sup>12</sup>6<sup>4</sup>(L-cage), respectively), which is larger than the S-cage. The structure of gas hydrates mainly depends on the size and shape of enclathrated guest species. It is well known that H<sub>2</sub> is too small to generate any hydrates by itself except for a high pressure region of the GPa order [1], that is, H<sub>2</sub> almost never contribute to the stability of hydrate cage. On the other hand, CO<sub>2</sub> generates structure-I hydrate easily in the moderate condition [2, 3]. A new H<sub>2</sub> separation using gas hydrates [4,5] owes to this distinction of hydrate-cage stability.

In the present study, the isothermal phase equilibria ( $p$ - $y$  relation) for the ternary (H<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O) system in the presence of gas hydrate phase have been measured in a temperature range of 274.3 - 281.9 K and a pressure range up to 10 MPa. The obtained  $p$ - $y$  relations have been correlated by Soave - Redlich - Kwong equation of state under the assumption of pure CO<sub>2</sub> hydrate formation.

In order to make sure the propriety of the above assumption, the single crystal of gas hydrates prepared from gas mixtures of  $\text{H}_2 + \text{CO}_2$  have been analyzed by use of Raman micro-spectroscopy.

## 2. Experimental

### 2.1. Experimental apparatus

A schematic diagram of the experimental apparatus used in the phase equilibrium measurement is shown in Fig. 1. The inner volume and maximum working pressure of the high-pressure cell are  $150 \text{ cm}^3$  and 10 MPa, respectively. The cell has a set of windows for visually observing the phase behavior in the high-pressure cell. All of them are immersed in a temperature - controlled water bath. The contents are agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring.

A high-pressure optical cell (with a pair of sapphire window) for Raman micro-spectroscopy is essentially the same to the previous one [6]. The details are not mentioned here.

The equilibrium temperature was measured within an accuracy of  $\pm 0.02 \text{ K}$  using a thermistor probe (Takara D-632), which was inserted into a hole in the cell wall. The probe was calibrated with a Pt resistance thermometer. The system pressure was measured by the pressure gauge (Valcom VPRT) calibrated by a RUSKA quartz Bourdon tube gauge within an accuracy of  $\pm 0.01 \text{ MPa}$ .

### 2.2. Experimental procedures

The  $\text{H}_2$  and  $\text{CO}_2$  mixture prepared at a desired composition was introduced into an evacuated high-pressure cell. The contents were pressurized up to a desired pressure by supplying water successively and then continuously agitated using a mixing bar. After

the formation of gas hydrates, the system temperature was kept constant to establish the three-phase coexisting state of hydrate + aqueous solution + gas. The phase behavior was observed straightforwardly through the window. After reaching the equilibrium state of three-phase coexistence, a small amount of gas phase was taken separately out for composition analysis. The equilibrium composition of gas phase was analyzed for H<sub>2</sub> and CO<sub>2</sub> by the TCD - Gas Chromatography (TCD-GC, Shimadzu GC-14B) as the H<sub>2</sub>O composition of gas phase is negligibly small under the present experimental conditions.

The single crystal of gas hydrate prepared from H<sub>2</sub> and CO<sub>2</sub> mixture was analyzed by *in situ* Raman spectroscopy by use of a laser Raman microprobe spectrometer with a multichannel CCD detector. The laser beam from the object lens was irradiated to the sample through the upper sapphire window. The backscatter of the opposite direction was taken in with the same lens. The argon ion laser beam (514.5 nm and 100 mW) and He-Ne laser beam (632.8 nm and 35 mW) were irradiated to the sample from the object lens. The spectral resolution was about 1 cm<sup>-1</sup>. The integration time was varied within the range 10 to 200 sec, depending on the intensity of the Raman scattering.

### 2.3. Materials

Research grade H<sub>2</sub> of purity 99.9999 % was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade CO<sub>2</sub> of purity 99.99 % was obtained from the Takachiho Tradings Co., Ltd. The distilled water was obtained from the Yashima Pure Chemicals Co., Ltd. All of them were used without further purifications.

## 3. Results and Discussion

The isothermal phase equilibrium ( $p$ - $y$ ) relations for the  $\text{H}_2 + \text{CO}_2 + \text{H}_2\text{O}$  system containing gas hydrate at 274.3, 276.5, 280.1, and 281.9 K are summarized in Table 1, and shown in Fig. 2. The three-phase equilibrium pressure increases monotonically with the composition of  $\text{H}_2$ . The variation of equilibrium pressure with the  $\text{H}_2$  composition exhibits similar behavior in the whole temperature range of the present study. The experimental data for the pure  $\text{CO}_2$  hydrate (left axis in Fig. 2) agree well with the previous ones [2, 3]. If a gas hydrate generated from the  $\text{H}_2 + \text{CO}_2$  mixture is the pure  $\text{CO}_2$  hydrate, the  $\text{H}_2$  is only like a diluent gas. That is, the  $\text{CO}_2$  hydrate is generated at considerably high total pressures where the  $\text{CO}_2$  fugacity in the gas mixture exceeds the equilibrium fugacity of pure  $\text{CO}_2$  hydrate system. The equilibrium fugacity of pure  $\text{CO}_2$  hydrate is calculated from the experimental data obtained in the present study. The equilibrium fugacity of pure  $\text{CO}_2$  hydrate is correlated by Equation (1).

$$f = a \exp(b \Delta T) \quad (1)$$

where  $a = 0.975$  MPa,  $b = 0.108 \text{ K}^{-1}$  and  $\Delta T$  stands for the deviation of temperature from the quadruple point [12] of hydrate + ice + aqueous solution + gas. It is assumed that the molar volume of  $\text{CO}_2$  hydrate is unchangeable.

At a given temperature and gas-phase composition, the total pressure is obtained by numerical calculation in order to give the equilibrium fugacity of pure  $\text{CO}_2$  hydrate. The fugacity coefficient of  $\text{CO}_2$  in the gas mixture is calculated by the Soave - Redlich - Kwong equation of state [11] with the ordinary mixing rule ( $k_{12} = -0.3426$ ) [8]. The critical constants of  $\text{CO}_2$  and  $\text{H}_2$  and other parameters in the reference [7] were adopted. The estimated results agree well with the experimental equilibrium pressures as shown in Fig. 2.

Raman spectra of the intramolecular vibration of  $\text{H}_2$  and  $\text{CO}_2$  at 274.6 K and 15.2

MPa are shown in Fig. 3(a) and (b). In order to avoid the optical effect of sapphire window, the spectra of CO<sub>2</sub> are given by the irradiation of the Ar ion laser, on the other hand, the spectra of H<sub>2</sub> are by the He-Ne laser. The Raman peaks of the intramolecular symmetric C=O stretching vibration mode of CO<sub>2</sub> are detected in both gas and hydrate phases and the spectra exhibit the double peaks because of the Fermi resonance effect. There is no significant difference from the Raman shifts of pure CO<sub>2</sub> hydrate [6] at the same pressure. On the other hand, the Raman peak of the H-H stretching vibration mode of H<sub>2</sub> is detected in the gas phase, while it is not detected in the hydrate phase. According to Mao *et al.* [9] and Mao and Mao [10], H<sub>2</sub> and H<sub>2</sub>O mixtures generate the structure-II hydrate at the high-pressure of 200 MPa or the low temperature of about 80 K, where the hydrate cages are multiply occupied with a cluster of two H<sub>2</sub> molecules in the S-cage and four H<sub>2</sub> molecules in the L-cages. The peak corresponding to such H<sub>2</sub> cluster is not detected in the single crystal of gas hydrate prepared from the H<sub>2</sub> + CO<sub>2</sub> mixture in the present study.

The above results reveal that H<sub>2</sub> is not enclathrated in hydrate-cages and behaves only like the diluent gas toward the formation of CO<sub>2</sub> hydrate. At a given temperature, the CO<sub>2</sub> fugacity of gas phase in equilibrium with liquid phase and CO<sub>2</sub> hydrate is calculated from the three-phase coexisting curve of pure CO<sub>2</sub> hydrate. The equilibrium pressure of gas mixture is uniquely obtained at given temperature and mole fraction of gas phase from the above assumption. Therefore, it is possible to estimate the equilibrium pressure - temperature - composition relations by extrapolating the experimental data under the CO<sub>2</sub>-fugacity-constant conditions. The estimated equilibrium pressure - temperature projections in this system are shown in Fig. 4. Four curves in Fig. 4 stand for the constant composition of gas phase. The operation temperature of separation process can be estimated under a desired pressure and composition. For example, in order to purify the H<sub>2</sub> + CO<sub>2</sub> mixture into  $y_{H_2}=0.90$  or

0.95 at 40 MPa, the operation temperature of separation process is about 275 K or 281 K, respectively.

#### **4. Conclusions**

Phase equilibrium relations for the ternary system of  $H_2 + CO_2 + H_2O$  in the presence of hydrate phase have been investigated. The gas hydrate prepared from the  $H_2 + CO_2$  mixture has been analyzed by use of Raman spectroscopy. The results reveal that  $H_2$  is not enclathrated in the hydrate-cages. That is,  $H_2$  behaves only like a diluent gas toward the formation of  $CO_2$  hydrate. It is possible to estimate the three-phase equilibrium relations ( pressure - temperature - composition ) of gas hydrate prepared from the  $H_2$  mixtures.

#### **Nomenclatures**

*f*: fugacity (Pa)

*k*: binary parameter for Soave-Redlich-Kwong equation of state

*p*: pressure (Pa)

*T*: temperature (K)

*y*: composition of gas phase

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## Figure captions

Fig. 1 Schematic diagram of experimental apparatus for the phase equilibrium measurement

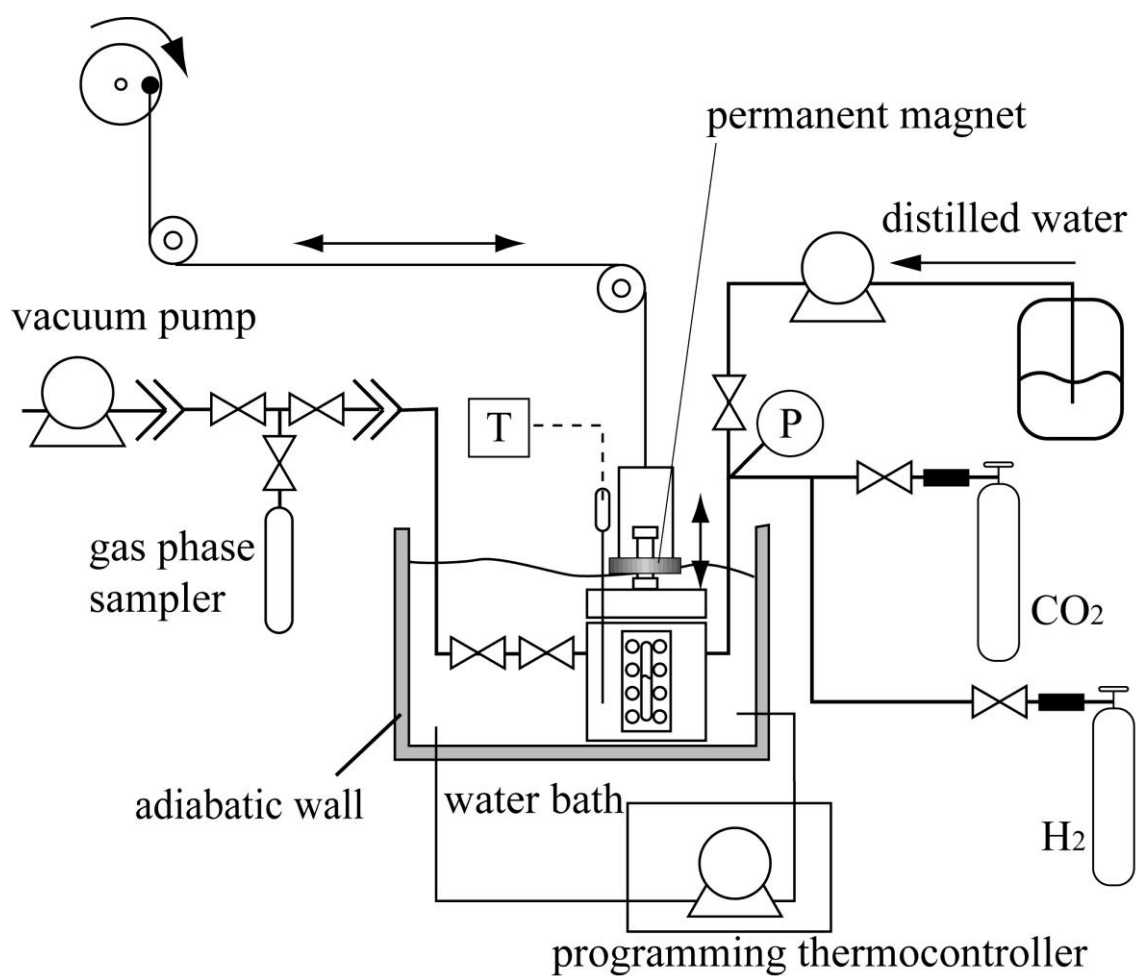
Fig. 2 Isothermal phase equilibrium (pressure - composition) relations for the  $\text{H}_2 + \text{CO}_2 + \text{H}_2\text{O}$  system in the presence of gas hydrate phase

Fig. 3 Raman spectra of the intramolecular vibration for  $\text{H}_2$  (a) and  $\text{CO}_2$  (b) molecules in the gas and hydrate phases. Raman peaks from  $4120$  to  $4150 \text{ cm}^{-1}$  are due to the sapphire window of the high-pressure optical cell.

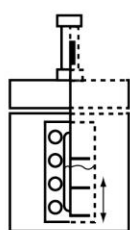
Fig. 4 Pressure - temperature projection estimated by Soave - Redlich - Kwong equation for the  $\text{H}_2 + \text{CO}_2 + \text{H}_2\text{O}$  system in the presence of gas hydrate phase

Table 1 Isothermal phase equilibrium data for the H<sub>2</sub> + CO<sub>2</sub> +H<sub>2</sub>O system in the presence of gas hydrate phase

	$y_{H_2}$	$p / \text{MPa}$		$y_{H_2}$	$p / \text{MPa}$
$T=274.3 \text{ K}$	0.000	1.42	$T=276.5 \text{ K}$	0.693	7.15
	0.140	1.75		0.704	7.46
	0.282	2.23		0.715	7.90
	0.352	2.42			
	0.568	3.58	$T=280.1 \text{ K}$	0.000	2.86
	0.697	5.49		0.061	3.06
	0.734	6.16		0.084	3.21
	0.805	8.89		0.173	3.71
				0.345	4.98
$T=276.5 \text{ K}$	0.000	1.81		0.405	5.35
	0.086	1.99		0.407	5.46
	0.190	2.49		0.435	5.67
	0.329	2.96		0.456	5.97
	0.455	3.46		0.508	6.51
	0.481	3.73		0.549	7.70
	0.497	3.93		0.577	8.69
	0.502	4.01		0.609	9.13
	0.530	4.10			
	0.551	4.48	$T=281.9 \text{ K}$	0.000	3.70
	0.566	4.58		0.134	4.50
	0.594	5.23		0.205	5.30
	0.651	6.21		0.340	6.73
	0.664	6.54		0.484	8.71

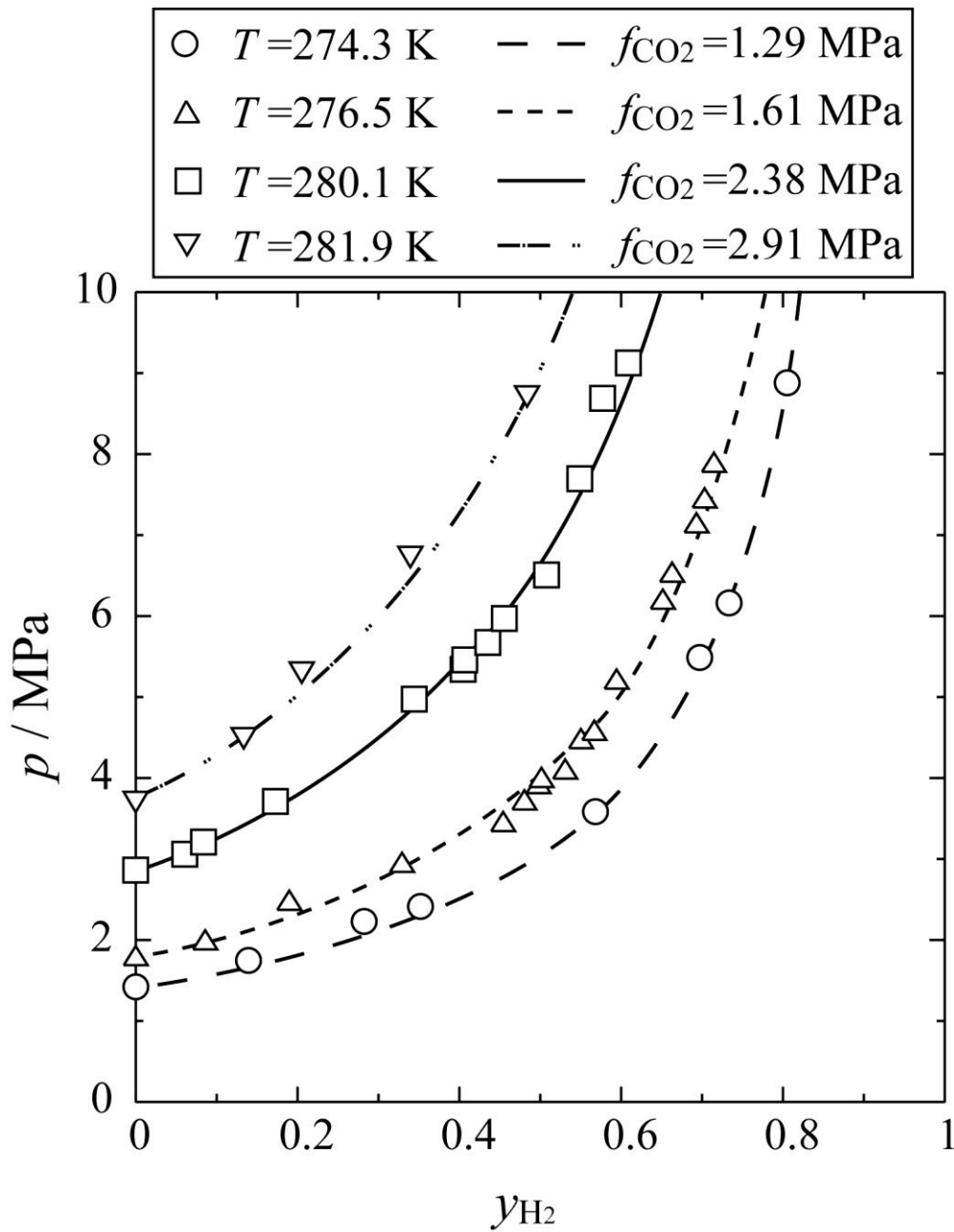


(P) pressure gage ( $\pm 10$  kPa) [T] thermometer ( $\pm 0.02$  K)

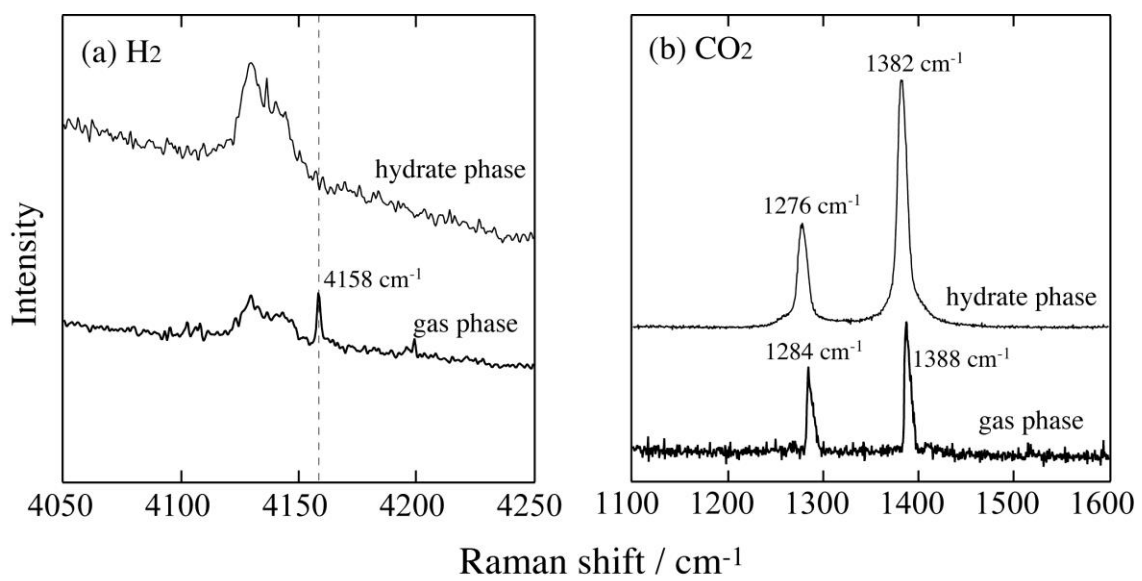


high pressure cell  
(inner volume: 150 cm<sup>3</sup>, maximum pressure 10 MPa)

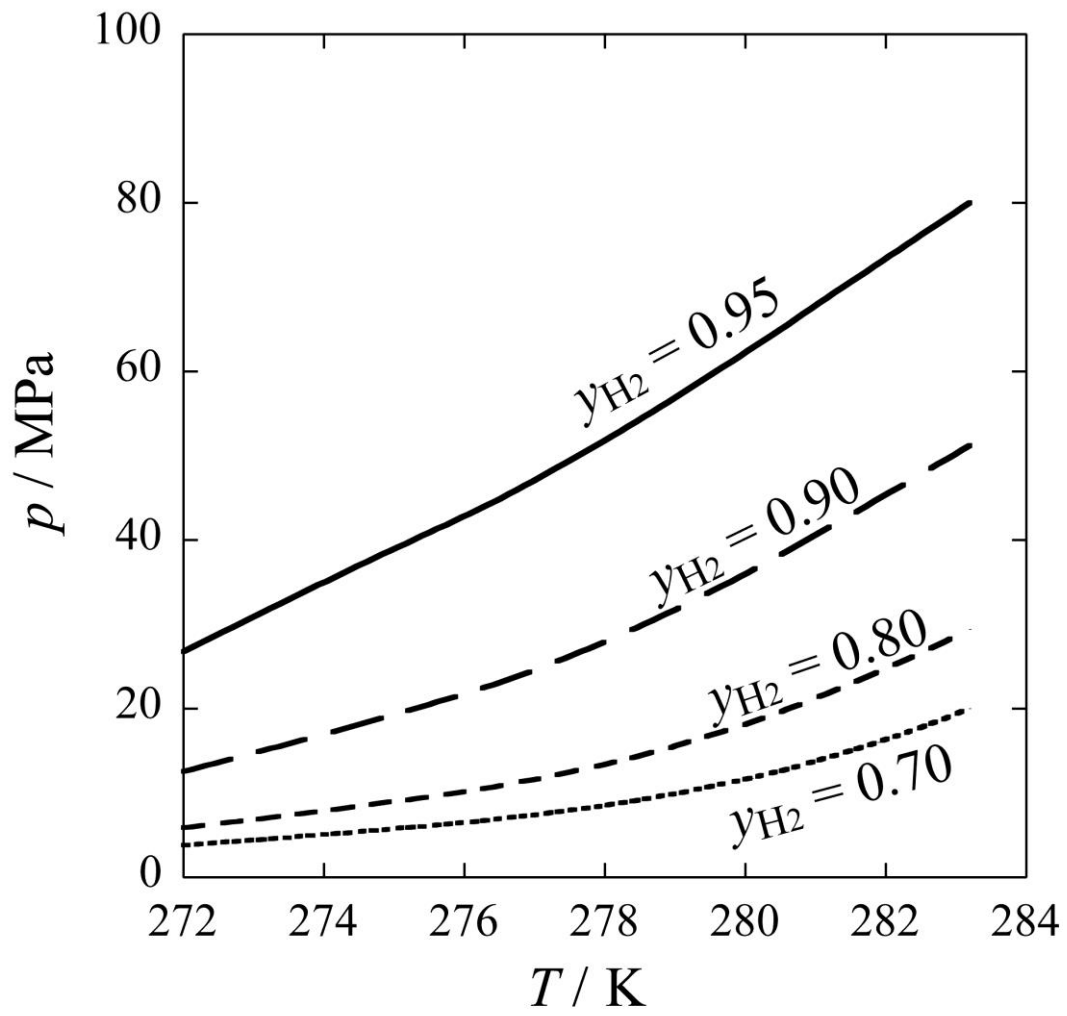
Sugahara *et al.*, Figure 1



Sugahara *et al.*, Figure 2



Sugahara *et al.*, Figure 3



Sugahara *et al.*, Figure 4