COMBINATION OF THE ISOCHORIC METHOD AND THE EXPANSION METHOD TO DETERMINE DENSITIES OF HYDROGEN AT TEMPERATURES UP TO 500°C

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Abstract -- *Utilization of hydrogen as an alternative fuel is promising because it is environmentally friendly. Hydrogen system design requires accurate hydrogen densities. The density of hydrogen is determined based on experimental data. For gases that have a low density such as hydrogen, the effective measurement method is required. An apparatus has been designed to measure PVT properties of hydrogen at pressures up to 1 MPa and temperatures up to 500ºC. The apparatus uses a combination of isochoric and expansion methods. The method doesn't need a measurement of pressures and temperatures along the isochoric line as required usually in the isochoric conventional method. Moreover, it doesn't need direct measurements of gas mass and gas volume. The volume was determined by measuring nitrogen at a pressure of 0.5 MPa and at temperatures up to 500ºC and by using Span's equation of state. Measurements of hydrogen have been performed at a pressure up to 0.7 MPa and temperatures up to 498.217ºC. Densities of hydrogen obtained from the present measurement are compared with that obtained from calculation of Leachman's equation of state. Maximum deviation is 1.42% at a temperature of 498.217ºC and at a pressure of 0.2947 MPa and minimum deviation is 0.11% at temperature and pressure of 399.461ºC and 0.6981 MPa respectively.*

INTRODUCTION

Hydrogen is expected to be alternative energy to replace fossil fuels. Utilization of hydrogen as a fuel produces no emissions and environmentally friendly. Safe utilization of hydrogen requires system planning in accordance with safety standards. Availability of accurate data on physical properties particularly related to pressure, volume, and temperature (PVT) is essential. Summary of the hydrogen PVT properties has been reported by the previous researchers (Jacobsen et al., 2007).

The hydrogen PVT properties can be determined experimentally by situating a certain amount of hydrogen in a high-temperature small tube. The volume of the tube was determined in advance. The hydrogen in the tube is then expanded into a vessel having a larger volume than its temperature is kept constant and the certain successive procedures were required to determine the hydrogen PVT properties. By using this method, the hydrogen has been measured from low up to elevated temperatures and pressures (Bartlett et al.,1928; Bartlett et al.,1930; Wiebe & Gaddy, 1938).

Extended range of measurements of hydrogen PVT properties in term of pressures and temperatures had been performed by other researchers (Michels & Goudeket, 1941; Michels et al., 1959). A wider range of temperature of measurements of hydrogen PVT properties also has been performed to provide data of the hydrogen PVT properties at higher temperatures (Presnall, 1969). Meanwhile, for parahydrogen, PVT properties data from the triple points and at up to elevated pressures have been reported by (Weber, 1975).

Although hydrogen experimental data have been published in a wide range of temperatures and pressures, however, experiment data of hydrogen PVT properties at temperatures above 150°C and pressures between 0.1 MPa and 1 MPa are insufficient.

An apparatus has been designed to measure hydrogen PVT properties at pressures and temperatures up to 1 MPa and 500°C. The apparatus uses a simple procedure. By using the apparatus, hydrogen is measured at temperatures of 300°C, 400°C, and 500°C and pressures of 0.3 MPa, 0.5 MPa, and 0.7 MPa. The densities of hydrogen obtained from the measurements are compared with that obtained from a calculation by using Leachman's equation of state (Leachman et al., 2009). The calculation results of hydrogen densities by using the equation of can be accessed on NIST webbook.

MATERIALS AND METHOD

The design of the apparatus in this study uses a combination of the isochoric method and the expansion method. The method does not require measurement of pressures and temperatures of the gas sample along the isochoric line as it does in conventional isochoric methods. Direct measurements of the mass and volume of gas samples are also not required in the determination of gas density. A combination of isochoric method and the expansion method uses two cells named sample cell (A) and expansion cell (B) and three valves K1, K2 and K3 respectively, as illustrated in Fig. 1.
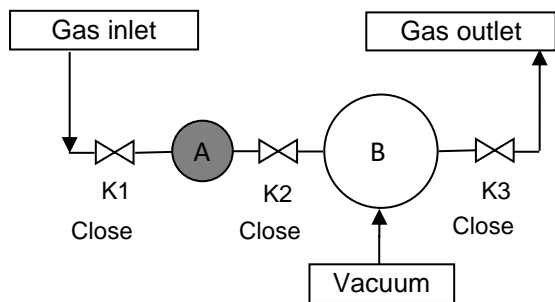
a. Before the expansion
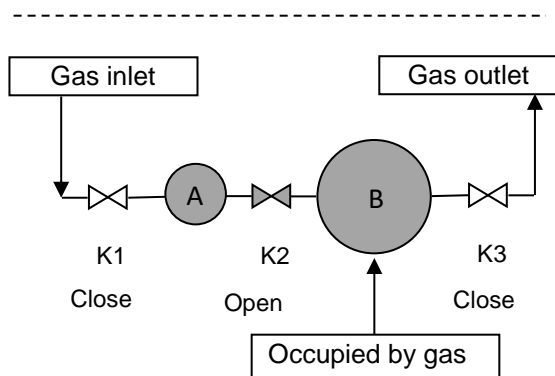
b. After the expansion
Figure 1. The combination of the isochoric and the expansion methods

The sample cell and expansion cell are evacuated in advance before performing a gas measurement. Fig. 1.a shows a condition after inserting the gas sample into the sample cell. The expansion cell is still in a vacuum condition. The gas mass in the sample cell is m_0. In this condition, the temperatures at both cells are maintained in the constant condition. Then temperature and pressure in the sample cell and the expansion cell are measured.

The gas sample is then expanded into the expansion cell by opening the K2 valve (Fig. 1.b).

Some of the gas will occupy the expansion cell. The gas mass inside the sample cell and the expansion cell after opening K2 valve are m_A and m_B respectively. After expanding the sample gas, the condition in the sample cell and the expansion cell are maintained until the pressure and temperature reach stability both in temperature and pressure. Furthermore, measurements of pressure and temperature on both cells are performed.

The amount of gas mass in the sample cell (m_A) and expansion cell (m_B) after opening K2 valve are equal to the gas density before the expansion (m_0). From Fig. 1, the mass equilibrium of the gas sample before and after the expansion is described in Equ. (1) – Equ. (3).

$$m_0 = m_A + m_B \tag{1}$$

$$\rho_0 V_A = \rho_A V_A + \rho_B V_B \tag{2}$$

$$\rho_0 = \rho_A + \rho_B \frac{V_B}{V_A} \tag{3}$$

The ratio of the volume of the expansion cell and the sample is determined by using Equ. (4).

$$\frac{V_B}{V_A} = \frac{\rho_0 - \rho_A}{\rho_B} \tag{4}$$

Sample cell and expansion cell are cylindrical shapes. The volumes of the sample cell and expansion cells are 250 cm^3 and 2500 cm^3 respectively. Both cells are made of stainless steel 316 (SUS316). The material is chosen because of its resistance to high pressure and high temperature, and it is also a good conductor material so that the temperature stability can be achieved rapidly. The volume of the expansion cell is designed much larger than that of the sample cell as it is expected that hydrogen pressure in the cells after the expansion becomes very low so that hydrogen can be treated as an ideal gas (Cengel & Boles, 2015; Motomura et al.,2010).

The sample cell and expansion cell are connected with a capillary tube of 0.4 mm in diameter. A valve is installed in between. The valve is used to control the gas flow from the sample cell to the expansion cell as shown in Fig. 1.

Pressure on the sample cell was measured by using a pressure transducer (Paroscientific model 2300A-101) which has a maximum measuring pressure of 2 MPa. The pressure in the expansion cell is measured with a similar device. The connection between the pressure transducer with the sample cell and the pressure transducer with the expansion cell is a 0.4 mm in diameter capillary tube. Each pressure transducers are connected to digital pressure indicators

respectively (Paroscientific Model 735). Furthermore, the pressure indicators are connected to the computer. The data obtained from the experiment are automatically stored in computer hard disk by using the LabVIEW® facility.

The sample cell is heated by using three heaters. The position of each heater is located at the top, middle, and bottom of the sample cell respectively. Each heater requires 2 kW of power. The temperatures of the heaters can be adjusted up to 500°C. A set of proportional-integral-derivative (PID) systems are used to control the temperatures of the heaters. The sample cell is covered by an insulating material to minimize heat transfer rate of the sample cell into the environment. Then the insulating material is placed into an airtight container. The utilization of container is aimed to avoid hydrogen leaking into the environment.

The container is equipped with a gas flushing system using nitrogen. This system is required to anticipate accumulation of hydrogen gas in the container if hydrogen gas leaking occurred from the sample cell to the airtight container.

The cooling system of the sample cell is performed by flowing pressurized air into the pipe which is placed around the sample tube. The cooling system is necessary to accelerate temperature decreasing of the sample cell after measuring at high temperature. The sample cell section detail is as in Fig. 2.

The temperature of the expansion cell is maintained by immersion it into hot water. Water temperature is maintained at constant temperature by using PID system. Water is heated using a heating element with 2 kW power. Water temperature was maintained at 70°C during the measurement.

Temperatures of the sample cell and the expansion cells are measured by using 25Ω Standard Platinum Resistance Thermometer (SPRT) model NSR 660. SPRT is connected to the Automatic System Laboratories Precession Thermometer Resistance Bridge (AΣΛ model F700B) equipped with a standard resistor (TINSLEY model 5648), and the resistance bridge is connected to the computer.

The SPRT is placed near the sample cell as shown in Fig. 2. While the expansion cell, the SPRT is immersed in hot water. BothSPRTs are placed at a distance as close as possible to the two cells to ensure high accuracy of temperature measurements. The temperature stability during measurement in the sample cell and the expansion cell is estimated to be ± 10 mK.

The gas feeding system uses four manifolds that can supply hydrogen, nitrogen, argon, and pressurized air. Each manifold is equipped with a manometer which is used to control the gas pressure supplied into the system. The maximum pressure gas that can be supplied into the system is 1 MPa.
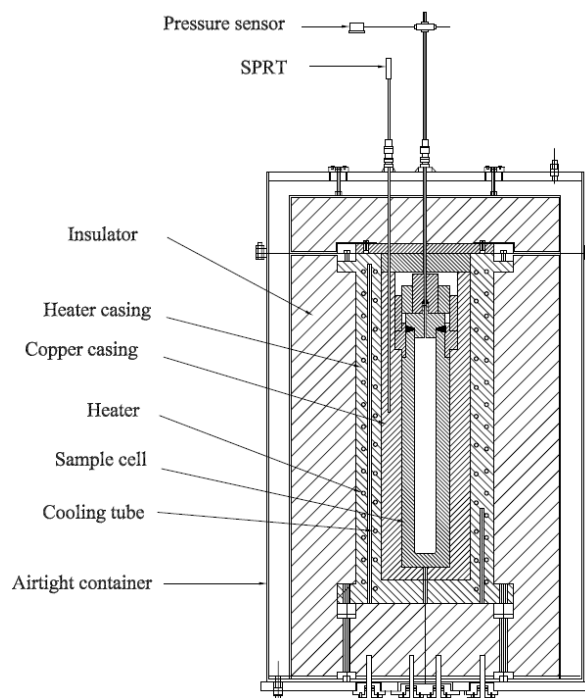

Figure 2. Detail of the sample cell section

The Apparatus is equipped with a gas evacuation system. The evacuation system is used to get a vacuum inside the sample cell and the expansion cell. Evacuating the system uses a vacuum pump (ULVAC model UTM150/T9B). The vacuum pump is connected to the gas outlet (Fig. 1.)

The hydrogen measurement begins with flushing the sample cell, the expansion cell, and the connecting pipes five times using nitrogen gas. Furthermore, the nitrogen inside the cells is evacuated using a vacuum pump for approximately one and a half hours. This process is very important to avoid contamination of hydrogen inside the cells with other gases. After the pressure inside the vacuum tube, the K1, K2, and K3 valves are closed (Fig. 1.a).

Parallel with the evacuation of nitrogen from inside the cells, the heating elements are switched on and set at 300°C for sample cell and at 70°C for expansion cell.

Hydrogen is filled into the sample cell through the gas inlet until the pressure inside the tube achieved 0.3 MPa. To achieve constant

pressure and temperature conditions on the sample cell, it takes about 5 minutes after the hydrogen filling process. Once the condition is stable, the hydrogen pressure and temperature in the sample tube are measured during 10 minutes. The hydrogen is then expanded into the expansion cell by opening the K2 valve and allowed to reach the stability of pressure and temperature on the sample cell and expansion cell. Furthermore, pressures and temperatures in the sample cell and the expansion cell are measured for 10 minutes.

In this study, at the sample cell, there are three temperature targets of measurement of hydrogen. They are 300°C, 400°C, and 500°C respectively and three targets of pressure measurement of 0.3 MPa, 0.5 MPa, and 0.7 MPa respectively. For the other measurement targets, the same procedure is used when measurement of hydrogen at temperature and pressure of 0.3 MPa and 300°C.

When hydrogen was measured at 300°C, there was a slight pressure drop in the sample cell before the expansion. The same conditions also occurred when measuring hydrogen at temperatures of 400°C and 500°C. From the observation, it was found that the pressure drop was getting bigger at a higher temperature.

Sever l efforts have been performed to find out the cause of the hydrogen pressure drop in the sample cell, among others, by checking pipe connection and detecting it using a hydrogen sensor, however, no leakage was found. The drop-in pressure in the sample cell was also experienced by previous researchers (Presnall, 1969). The sample cell material used in the Presnall study differs from the sample tube material in this study.

As a comparison, the apparatus in this study was also used to measure helium and nitrogen gas. Measurements were performed at temperatures up to 500°C. The observation during measurements shows that there are no pressure drops in the sample cell, although the measurement of helium and nitrogen has reached up to 500°C. It is concluded that pressure drop at elevated temperatures only occurred in hydrogen measurements.

The constant pressure conditions in sample cell are difficult to achieve when measuring hydrogen at elevated temperatures. The measurement method states that the gas mass in the expansion cell and the sample cell after the expansion is equal to the gas mass in the sample sell before the expansion. Therefore, to meet the equilibrium equation as in Equ. (1), then the expansion is performed as soon as possible after measuring of pressures and temperatures on the

sample cell. The results show that the hydrogen gas pressure in the sample cell and the expansion cell becomes very low after the expansion.

RESULTS AND DISCUSSION

Fig. 3 shows the volume ratio of the expansion cell and the sample cell. The ratio is determined by measuring nitrogen at a pressure of 0.5 MPa and a temperature from 100°C up to 500 °C. The nitrogen measurement procedure uses the same procedure as hydrogen measurements.

The changes in cell volume in the apparatus are assumed only caused by temperature changes since the measurements are performed at low pressure. The volume of the capillary tube between the sample cell and the expansion cell is also involved in determining the volume ratio.
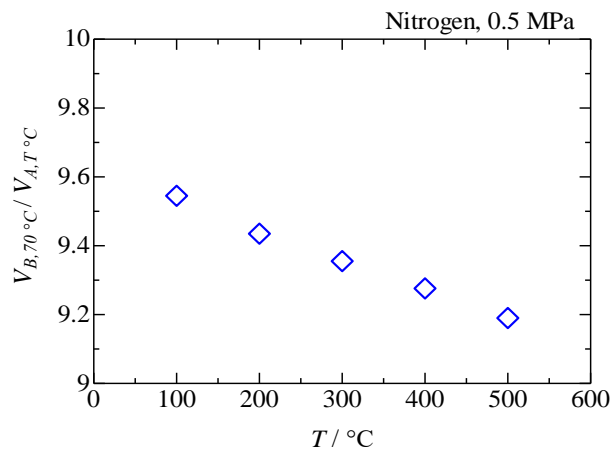
Figure 3. The volume ratio of the expansion cell and the sample cell

The data obtained from nitrogen measurements are merely in the form of pressure and temperature at the sample cell and the expansion cell. The densities of nitrogen are obtained from the calculation of the Span's equation of state which refers to temperatures and pressures of measurement (Span et al., 1998). Furthermore, by using the nitrogen densities, the volume ratio of the expansion cell and the sample cell is determined by using Equ. (4).

Table 1. Ratio volume of the expansion cell and the sample cell.

$V_{B,70°C}/V_{A,300°C}$	$V_{B,70°C}/V_{A,400°C}$	$V_{B,70°C}/V_{A,500°C}$
9.3552	9.2759	9.1898

Table 1 shows the volume ratio between the expansion cell and the sample cell. The increment of temperature from 300°C to 400°C leads to a decreasing of the sample cell volume by 0.85%

and from a temperature of 300ºC to 500ºC leads to that of the sample cell by 1.7%.

Table 2. Measurement results of hydrogen

T (ºC)	P (MPa)	ρ_{exp} (mol.dm^{-3})
299.983	0.3006	0.0633
299.987	0.5002	0.1055
299.987	0.7003	0.1470
399.456	0.2990	0.0539
399.445	0.4995	0.0898
399.461	0.6981	0.1247
498.217	0.2947	0.0466
498.208	0.4918	0.0776
498.209	0.6922	0.1088

The purity of hydrogen in the present measurement is 99.999%. Table 2 shows the densities of the hydrogen from measurement results at targeted pressures and temperatures. The first and second columns are obtained from the measurement results. The third column is calculated by using Equ. (3). The densities of hydrogen in the sample cell and the expansion cell as required to calculate the Equ. (3) are obtained from the calculation using ideal gas equation. The ideal gas equation is used because after the expansion process the hydrogen pressure in the sample cell and the expansion cell becomes very low so that it can be treated as an ideal gas.
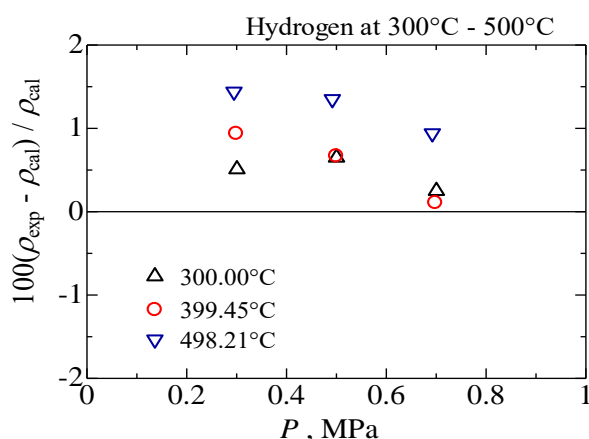

Figure 4. Deviation of the present measurement with Leachman'sequation of state

The temperatures as presented in Table 2 are the average values of the temperature throughout the measurement. Temperature stability can be achieved by the measurements. While for the pressure as presented in the second column of Table 2 are data of the final measurements of pressure shortly before the expansion process are performed, as the measurement of high temperature, the pressure on the sample cell slightly decreased with time. This procedure is taken to satisfy the equilibrium of mass as stated in Equ. (1).

Fig. 4 shows the deviation between the densities obtained from the measurement results with densities which calculated from Leachman's equation of state. The maximum deviation of the measurement results with calculated density is 1.42% at a pressure of 0.2947 MPa and at a temperature of 498.217ºC and minimum deviation of 0.11% at a pressure of 0.6981 MPa and a temperature of 399,461ºC. The tendency shows that at higher temperatures the deviation is bigger.

CONCLUSIONS

An Apparatus to measure PVT properties of hydrogen at pressures and temperatures up to 1 MPa and 500°C has been designed. The apparatus uses a combination of the isochoric and the expansion method. Hydrogenattemperatures of 300°C, 400°C, 500°C, and at pressures from 0.3 MPa up to 0.7 MPa has been measured.

The densities obtained from the present measurement are compared with densities which obtained from calculation of the Leachman's equation of state. The maximum deviation of the measured density with calculated density is 1.42% at 498.217ºC and at a pressure of 0.2947 MPa and a minimum deviation of 0.11% at temperatures and pressures of 399.461ºC and 0.6981 MPa, respectively.

NOMENCLATURE

P	: Pressure
T	: Temperature
V	: Volume
m	: Sample mass
ρ	: Density

Subscript

A	: sample cell
B	: Expansion cell
0	: Before the expansion
exp	: Experiment
cal	: calculation

ACKNOWLEDGMENT

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