Realization of the Triple Point of Equilibrium Hydrogen Using an Open Cell and a GM Closed-Cycle Refrigerator

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Abstract: The triple point of equilibrium hydrogen is realized by adiabatic calorimetry using an open cell and a closed-cycle helium refrigerator. The heat capacity anomaly is observed at temperatures of about 0.1 K below the triple point of equilibrium hydrogen when using 2 g of activated ferric oxy-hydroxide as a catalyst for the equilibration of ortho- and para-hydrogen against about 0.1 mol of hydrogen. It is confirmed that the anomaly is caused by the interaction between hydrogen and the catalyst. The anomaly is, however, reduced within the accuracy of measurements by decreasing the amount of the catalyst, such as about 0.17 g against about 0.1 mol of hydrogen. In the latter case, it takes about 3 days for equilibration of ortho- and para-hydrogen and relatively flat melting curves are obtained.

Key Words: triple point of hydrogen, heat capacity anomaly of hydrogen, GM refrigerator, ITS-90

1. Introduction

The triple point of equilibrium hydrogen is one of the defining fixed points for calibrating the interpolation instruments defined by the International Temperature Scale of 1990 (ITS-90)^{1)~4)}, the temperature of which is assigned as 13.8033 K. The triple point of equilibrium hydrogen is required for the low temperature standards; it is the lowest calibration fixed point for standard platinum resistance thermometers and is also one of three fixed points to calibrate the interpolation gas thermometer adopted by the ITS-90 in the range from the vapor pressure point of helium to the triple point of neon (24.5561 K).

Hydrogen is a mixture of two molecular isomers, orthohydrogen and para-hydrogen. The fraction of these isomers at equilibrium depends on temperature. At room temperature the equilibrium composition is 75% orthohydrogen and 25% para-hydrogen, which is called as "normal hydrogen". However, at 14 K the equilibrium hydrogen contains less than 0.1 % or tho-hydrogen. On the other hand, the natural conversion rate between orthoand para-hydrogen is very slow⁵⁾. The triple point temperature of equilibrium hydrogen is about 0.15 K lower than that of normal hydrogen. This compulsorily requirs to equilibrate ortho- and para-hydrogen in realizing the triple point of equilibrium hydrogen. As the triple point of equilibrium hydrogen was adopted as one of the defining fixed points of the International Practical Temperature Scale of 1968, the equilibration techniques between ortho-hydrogen and para-hydrogen were already established ^{4), 6), 7)}, i.e. it is recommended to use a catalyst for equilibration, such as activated ferric oxy-hydroxide, and to fill the fixed point cell with a catalyst to reduce uncertainties from non-equilibration of ortho- and parahydrogen.

Many reports had been published about the characteristics of the triple point of hydrogen $^{4), 6)\sim 8)}$. The most of them were realized by a cryostat using liquid helium and by applying a quasi adiabatic method. In such a helium bath type cryostat, the temperature distribution inside the cryostat depends largely on the liquid level of helium. This makes it difficult to design a precise adiabatic calorimeter for the fixed point realization without disturbing an adiabatic condition for a long measuring time. It may be one of main reasons to use a quasi adiabatic method for a helium bath system.

On the other hand the mechanical cooling system had not been used in the field of temperature standards. However, recently, applying a closed cycle refrigerator to the fixed point realization combining with sealed cells, successful results were reported $^{5),9),10)}$. The temperature distribution inside the cryostat of a mechanical cooling system depends mainly on the cooling power of the refrigerator. It means that the temperature distribution inside the cryostat is stable for a long time, which is suitable for an adiabatic calorimetric system. Based on these we proposed to use a mechanical cooling system for the realization of the low temperature fixed points combining with an adiabatic calorimetric method. Some fixed points were demonstrated to be easily realized $^{5),9)}$. As the results of precise adiabatic calorimetric measurements of hydrogen, a heat capacity anomaly was discovered at temperatures

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Fig. 1 Schematic side view of the adiabatic calorimeter used for the heat capacity measurement and for the realization of the triple point of hydrogen.

near the triple point of hydrogen. The anomaly was suspected to be caused by a catalyst for ortho-para conversion As this anomaly was very close to the triple point, a warning was given that the anomaly does not only deform the melting curves but has a possibility to influence the triple point temperature $^{5), 9)}$.

There was no report in the past for such a heat capacity anomaly as those, although the triple point of hydrogen had been measured for more than a half century. To clarify the anomaly, the triple point of hydrogen was measured by an open cell in this experiment. An open cell is convenient to change the amount of the catalyst and hydrogen. To confirm the anomaly, the heat capacity of the cell with sample hydrogen was compared with that of the empty cell.

In this report we first confirm that the heat capacity anomaly is caused by the catalyst. Then we show how to reduce the anomaly in realizing the triple point of equilibrium hydrogen.

2. Equipment and measuring procedure

2.1 Equipment

A Gifford-McMahon (GM) type refrigerator with double cooling stages is used as cooling equipment, the lowest

temperature of which is about 7 K at the second stage. For the thermal equilibration between sample hydrogen and thermometers, a cylindrical copper block is used with a sample cell of about 4 cm³ in volume for the fixed point realization and with 6 thermometer wells for capsule type standard thermometers. A capillary with 2 mm in outer diameter, through which hydrogen at room temperatures is liquefied, is connected to the fixed point cell. As shown in **Fig. 1**, the cell block is covered with adiabatic radiation shields. They are covered with two other radiation shields connected to the first and second cooling stages. These structure of the cryostat is nearly the same as that used for a sealed cell⁵.

The copper block was cooled by thermal conduction through the capillary and leads. No heat exchange gas was used. The conventional cooling method using exchange gas was not applied to this system because it gives sometimes uncertainties in heat capacity measurement by adsorbed gases at the cell block. In addition, by cooling only through solid thermal conduction, the cold tip of the refrigerator is working as a sorption pump to residual gases. It is convenient for calorimetry to keep the adiabatic space in high vacuum.

To eliminate thermal conduction and radiation through the capillary from room temperatures, the filling capillary was anchored at the first cooling stage (about 70 K) and at the adiabatic radiation shields. The adiabatic radiation shields were cooled through stainless steel pipes connected to the 2nd cooling stages and leads anchored at the 2nd cooling stage. The lowest temperature of the adiabatic shields is determined by the balance of heat through these pipes and wires. The lowest temperature of the shields was about 10 K in the present cryostat.

A GM refrigerator has mechanical vibration at the cooling stages, which is one of the reasons not to be used in precise measurements. For sealed cells, it was easy to eliminate such vibration, as they were not required to be connected mechanically to the flanges of the refrigerator⁵⁾. For an open cell, the vibration of the refrigerator, however, comes through the capillary, which must be connected mechanically at some flanges. To reduce the vibration the capillary was connected only at the top flange, and the copper block was designed to have freedom in both horizontal and vertical directions as shown in Fig. 1. The copper braids were used as heat anchors at the radiation shields to eliminate the vibration of the refrigerator.

The temperature of the adiabatic radiation shields was controlled by a PID controller through amplified emf's of a series of three Chromel/gold-iron thermocouples thermally connected at the adiabatic radiation shields and at the comparison copper block. To reduce the temperature drift of the copper block during adiabatically controlling, the off-set voltage of the amplifier was adjusted.

Two capsule type rhodium-iron resistance thermometers and two platinum resistance thermometers were used in this experiment, the resistance of which was measured by Direct Current Comparator Bridges (Guildline 9975 and Measurement International/ISOTECH SW6010A/TTI3). The results obtained by a rhodium iron thermometer will be used for the discussion in this article. To estimate the self-heating effect by the exciting currents, the resistance was measured by two currents, i.e. 0.3 mA and $0.3 \times \sqrt{2}$ mA. From those two measurements the resistance of the thermometer at zero current was estimated if necessary.

Hydrogen with the nominal purity of better than 99.999999 % was used in this experiment. Ferric oxyhydroxide was used as a catalyst for equilibration of orthoand para-hydrogen. The catalyst was activated at temperatures above 150 $^{\circ}$ C in vaccum for several hours.

To confirm the thermal anomaly of hydrogen, about 2 g of ferric oxy-hydroxide was placed at the bottom of the fixed point cell and about 0.1 mol of hydrogen was lique-fied. To realize the triple point of hydrogen by reducing the heat capacity anomaly, about 0.17 g of the catalyst was placed in the cell. To eliminate residual gases in the cell, the cell was evacuated for about 24 h at room temperatures. Then the cell was filled with pure hydrogen gas of about 100 kPa. This condition was kept for a few hours before re-evacuation. The same procedure was repeated several times.

2.2 Measuring procedure

The temperature of the 2nd cooling stage reached below 10 K within 4 h after starting the operation of the refrigerator. It needed, however, about 3 days to cool the cell block below 14 K, as the cell was cooled through the heat conduction only of leads and the capillary. When the temperature of the cell block became below 14 K, pure hydrogen at room temperatures was liquefied in the cell through the capillary. To liquefy 0.1 mol of hydrogen it took about 3 h.

Both the heat capacity and the triple point were measured by an adiabatic calorimetric method. The procedure is as follows. The temperatures of the adiabatic radiation shields were always controlled so as to be the same as that of the fixed point cell throughout measurement. The resistance of the thermometer was measured after the temperature of the copper block became constant. A heat pulse was given to the cell through the heater wound around the cell block. The heat given to the sample and the cell was calculated from the currents of the heater and the EMF's between the potential leads of the heater. About 0.3 J was given by a heat pulse at temperatures below and above the triple point. At the triple point the heating period was adjusted depending on the fraction of melt. About 0.1 J to 0.5 J was given by a heat pulse depending on the fraction of melt.

To confirm thermal equilibrium, the resistance of the thermometer was measured for about 15 min, except at the triple point. At the triple point the period for thermal equilibration depends on the fraction of melt, F. The thermal equilibration was confirmed by monitoring the resistance of the thermometer. The resistance at the equilibrium was measured after the temperature drift of the cell block became positively larger than -0.05 mK/h. As the initial drift rate depended on the heater currents and the fraction of melt, the measurement of the drift rate was started at 15 min after a heat pulse. Near the end of the melting, i.e. $F \approx 1$, the drift of the copper block temperature depends not only on the phase equilibration but on the accuracy of the temperature controller of the adiabatic shields. It was difficult to confirm the thermal equilibration only by monitoring the drift of the temperature in the range blow $1/F \approx 1.5$. In this range the resistance of the thermometer was measured at about 60 min after giving a heat pulse.

Before filling the sample into the cell, the heat capacity of the empty cell including about 2 g of the catalyst was measured. Less than 0.1 mmol of hydrogen was filled in the cell for thermal contact between the cell block and the catalyst. In this experiment no heat capacity anomaly was observed.

After that about 0.1 mol of hydrogen was liquefied in the cell. By a liberation of ortho-para conversion heat, the cell temperature rises quickly to above 20 K. To keep the vapor pressure less than 100 kPa, the temperature of the cell was controlled to be below 20 K. After the equilibration of ortho- and para-hydrogen the heat capacity was measured to confirm the anomaly.

Next we tried to reduce the anomaly for the purpose of the realization of the triple point of equilibrium hydrogen. To reduce the heat capacity anomaly, the amount of the catalyst was adjusted. It was confirmed that the heat capacity anomaly was within the scatters of the present measuring accuracy by about 0.17 g of the catalyst against 0.1 mol of hydrogen. By decreasing the amount



Fig. 2 Heat capacity curve of the empty cell including about 2 g of ferric oxy-hydroxide.

of the catalyst the conversion rate of ortho-hydrogen to para-hydrogen became slow. It was not easy to detect the equilibration of hydrogen clearly from the temperature rise by a liberation of heat. The time dependency of the triple point temperature was measured to confirm the equilibration between ortho- and para-hydrogen.

3. Results and discussion

3.1 Heat capacity anomaly

First of all it was confirmed there is no anomaly in the heat capacity of the empty cell including about 2 g of ferric oxy-hydroxide. As shown in **Fig. 2**, the heat capacity curve is smooth against temperature and no heat capacity anomaly is observed at temperatures near the triple point. It means that the cell and the catalyst have no thermal anomaly and they at least satisfy the necessary conditions for the fixed point use.

Then about 0.1 mol of hydrogen was liquefied in the cell for the measurement of the heat capacity of equilibrium hydrogen. It took about 20 h for the equilibration of ortho- and para-hydrogen, during which was observed a temperature rise of the cell by a liberation of the conversion heat from ortho-hydrogen to para-hydrogen. When using a fixed point cell filled with a catalyst, it usually took less than 7 h for the equilibration. By 2 g of a catalyst, which is far smaller than the recommended amount of the catalyst, against 0.1 mol of hydrogen, more than two third of liquid hydrogen may not be directly interacting with the catalyst. Considering these situations the conversion period of 20 h may be reasonable.



Fig. 3 Heat capacities of about 0.1 mol of hydrogen with about 2 g of ferric oxy-hydroxide as a catalyst for the equilibration of ortho- and para-hydrogen at temperatures near the triple point including the cell block.

The heat capacity of hydrogen in this condition is shown in **Fig. 3**. In this figure the relation between temperature and the logarithmic heat capacity of hydrogen is given. The heat capacity anomaly is observed at temperatures of about 0.1 K below the triple point. As shown in this figure the anomaly is reproducible. Comparing this result with the heat capacity of the empty cell, the heat capacity anomaly is caused by the interaction between the catalyst and hydrogen. The peak temperature is closer to the triple point than that of the sealed cell⁵. The difference between those is supposed to be in the filling factor, the activation treatment and the density of a catalyst.

Even by about 2g of the catalyst, which is far less than the recommended value, the heat capacity anomaly is giving some influence on the melting curve as shown in this figure. From these results, the recommended method of the ITS-90 might give much larger influence on the triple point temperature of the equilibrium hydrogen.

3.2 Melting curve of hydrogen interacting with the catalyst

From Fig. 3 it is easy to imagine that the anomaly makes some distortion on the melting curves. The melting curve of the triple point of hydrogen interacting with the catalyst is shown in **Fig. 4**. In this figure is given the relation between the time of calorimetric measurement and the resistance of the rhodium iron thermometer. Double plateaux of the melting curve correspond to the heat capacity anomaly and the main melting. As the catalyst used in this experiment is not filled in the cell completely, the melting curve in Fig. 4 is that of the mixture of both interacting and non-interacting hydrogen with the catalyst.

The melting curves of hydrogen had been measured for more than a half century, but the anomaly had not been observed as clearly as shown in Fig. 3. It may be because the anomaly is close to the triple point and is overlapping with the premelting. It might be difficult for a quasi adiabatic system, which is not possible to make the sample thermally well equilibrate, to observe such critical phenomena as the anomaly observed in this experiment.

On the other hand a mechanical refrigerator and an adiabatic calorimeter were applied to this experiment. In using a mechanical refrigerator, there is no limitation of time in waiting for the equilibration of ortho-para conversion and for thermal equilibration. The system was also operated without exchange gas, which also makes thermal ambiguity negligibly small in heat capacity measurement. Such a precise calorimeter might reveal the heat capacity anomaly by discriminating two heat capacity peaks in such a small temperature range of a few 10 mK.

The mechanism of the heat capacity anomaly may be related to the interaction between the porus catalyst and hydrogen⁵⁾. However it may not be possible to be clarified only from the results of melting curve and heat capacity measurement. Other analysis may be necessary. In this report a warning will be given to the realization of the triple point of equilibrium hydrogen by the conventional method.

3.3 Realization of equilibrium hydrogen

To realize the triple point of equilibrium hydrogen, the equilibration of molecular isomers of ortho-hydrogen and para-hydrogen is inevitable. However, a thermal anomaly, such as shown in Fig. 3 at temperatures near the triple point, has a possibility to influence the triple point temperature. Generally in designing a furnace and/or fixed point cells, the cell material and thermal insulators will be selected so as not to have heat capacity anomalies at temperatures near the fixed points. It is not suitable for the triple point instruments to have such an anomaly as shown in Fig. 3.

However without a catalyst it is already reported that more than 4 months may be required to obtain equilibrium hydrogen and virtually it means that it is not possible to obtain equilibrium hydrogen. From Fig. 3, the anomaly is expected to depend on the amount of hydrogen interacting with the catalyst. By decreasing the interacting hydrogen, which is equivalent to use a small amount of a



Fig. 4 An example of the melting curves of hydrogen using about 2 g of ferric oxy-hydroxide as a catalyst against about 0.1 mol of hydrogen.

catalyst, the influence of the anomaly on the triple point temperature is expected to become small.

On the contrary, by decreasing the amount of a catalyst, the conversion rate becomes slow and it will take a long time to obtain equilibrium hydrogen. The balance between those will be required. By adjusting the amount of a catalyst, less than 0.2 g of ferric oxy-hydroxide was found to be one of the upper limits for both problems; the heat capacity anomaly is of the order of the scatters of measurement and its influence on the melting curves is negligibly small. When using less than 0.2 g of the catalyst, the conversion rate, however, became slow and it is not easy to confirm the equilibration of hydrogen from a liberation of conversion heat. In this experiment the changes of the triple point temperature, which depends on the composition of ortho- and para-hydrogen, were measured to confirm the equilibration of hydrogen.

Using about 0.17 g of the catalyst in about 0.1 mol of hydrogen, the time dependency of the triple point temperature is shown in **Fig. 5**. In this figure is given the relation between the resistance of the rhodium iron thermometer at the triple point and the time after liquefying hydrogen. As the interacting hydrogen might be a few percent of the total amount of hydrogen, it was suspected that it took a long time to complete the ortho-para conversion. However, the equilibrium hydrogen was obtained by about 3 days as shown in Fig. 5. The period of 3 days is acceptable for practical procedure in the field of precise measurement, as it takes about 3 days to cool down the



Fig. 5 Time dependency of the triple point of hydrogen measured by the resistance of the rhodium-iron thermometer using about 0.17 g of ferric oxy-hydroxide as a catalyst for the ortho-para conversion against 0.1 mol of hydrogen

system from room temperatures to 14 K.

Further in using less than 0.1 g of the catalyst, it seemed to be required for more than a week to equilibrate orthopara hydrogen. Even in this case, the influence on the melting curves of hydrogen by the catalyst may be a half of that at 0.2 g of the catalyst. So a little bit less than 0.2 g of the catalyst is reasonable for both the period of conversion and the melting curve measurements.

3.4 Heat capacity by a small amount of the catalyst

When using about 0.17 g of the catalyst against about 0.1 mol of hydrogen, the heat capacity of solid and liquid hydrogen is shown in **Fig. 6**. In this figure the heat capacity data of several runs are plotted and the heat capacities of the cell block and thermometers are subtracted. To clarify the anomaly, the scale of the vertical axis is expanded and the heat capacity at the triple point is out of the scale. As the measurement is very precise, the anomaly is still observed at closer temperatures to the triple point, but is not so large like Fig. 3. The difference of heat capacity between solid and liquid hydrogen can also be observed even for about 0.1 mol of hydrogen.

In cooling the cell, the temperatures of the adiabatic shields were not controlled, i.e. they were about 10 K, and thermal exchange gas was not used as mentioned above. The sample was solidified with the cooling rate of about -0.5 K/h, which is very slow compared with the traditional cooling method using exchange gas. The solid



Fig. 6 Heat capacity of 0.1 mol of liquid and solid hydrogen using about 0.17 g of ferric oxy-hydroxide. The data of the heat capacities do not include those of the cell and the thermometers. The sample is annealed at about 12.5 K for a few hours.

hydrogen by this cooling rate, however, showed the distortion of heat capacity curves at about 1 K below the triple point. The results of Fig. 6 are obtained using the sample annealed for about 2 h at temperatures of about 1 K below the triple point. By adopting this annealing treatment the distortion of the heat capacity curves disappeared. Even in the cooling speed of -0.5 K/h, there may be some distortion in the solid hydrogen, or hydrogen becomes amorphous and the annealing of solid hydrogen is required for the precise measurement of the triple point.

The results of Fig. 3 are also obtained by well annealed sample. Comparing these two figures, it is clear that the heat capacity anomaly is not caused by the distortion in the hydrogen crystal but is by some interactions between the catalyst and hydrogen around.

3.5 Triple point of equilibrium hydrogen

After the equilibration of ortho- and para-hydrogen as shown in Fig. 5, the melting curves of the triple point were measured. The results of the melting curves are shown in **Fig. 7**, where the relation between the inverse of fraction melted, 1/F, and the resistance of the rhodium iron thermometer is given. The data of several runs of measurements are plotted. The linear relationship is obtained in the range below 1/F = 14. The melting curves of hydrogen are flat within 0.2 mK in this range.

The equilibration of ortho- and para-hydrogen is confirmed by the reproducibility of the melting curves. It



Fig. 7 Melting curves of the triple point hydrogen against the inverse of the fraction of melt, 1/F. The vertical axis is the resistance of the rhodium iron thermometer

took about 30 h to obtain a complete melting curves. In addition to the melting curve measurement, it needs other 20 h to solidify, to anneal the sample and to measure the heat capacity at solid and liquid hydrogen. During this period, the drift of the triple point temperatures were not observed as shown in Fig. 7. It means the fraction of ortho- and para-hydrogen is not changed during this period. On the other hand without a catalyst, the melting temperature had been still drifting with the rate of about -0.05 mK/day after 4 months because of the conversion from ortho-hydrogen to para-hydrogen. From these results, the equilibration of ortho-hydrogen and para-hydrogen is possible to be obtained by using even a small amount of a catalyst.

4. Conclusion

In using ferric oxy-hydroxide as a catalyst for equilibration of ortho- and para-hydrogen, it is confirmed that the heat capacity anomaly exists at temperatures near the triple point and that it is caused by some interactions between the catalyst and hydrogen. By reducing the amount of the catalyst it is also confirmed that the heat capacity anomaly becomes negligibly small. From these results it is recommended that in realizing the triple point of equilibrium hydrogen a small amount of a catalyst should be used. However, as the conversion rate from ortho-hydrogen to para-hydrogen becomes small, it needs a long time to obtain equilibrium hydrogen.

In this experiment a mechanical refrigerator was applied to realize the triple point of condensed gas using an open cell. The system seems to be superior to the traditional liquid helium bath for precision measurement. The most advantageous point for calorimetry is that the temperature distribution inside the cryostat of the mechanical refrigerator is stable during operation. Further it is possible to operate all the system automatically. The system is suitable for such experiments with a long relaxation time as the equilibration of ortho-para hydrogen or phase transitions. By using these advantages, the heat capacity anomaly was first confirmed. It may be recommendable for temperature standards to use a mechanical refrigerator.

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