Realization of the Triple Points of Equilibrium Hydrogen and Equilibrium Deuterium

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New high pressure type of hydrogen sealed cells is designed and developed for realizing the triple point of equilibrium hydrogen, which is possible to replace sample gas without destruction. The triple point of equilibrium hydrogen has been realized using a calorimetric method and the new sealed cells, which include ferric hydroxide as a catalyst for the ortho-para equilibration. The triple point of equilibrium deuterium has also been realized using a sealed cell fabricated at Istituto di Metrologia G. Colonnetti, which include gadolinium oxide as a catalyst for the ortho-para equilibration. Anomalous increases on heat capacity curves of each substance, which markedly disturb melting curves of the triple point, are observed at temperatures just below the triple point. In the case of equilibrium hydrogen, a reduction of the amount of the catalyst suppresses the anomalous increases and allows one to obtain more reliable melting curves of the triple point.

Key Words: temperature, ITS-90, triple point of hydrogen, triple point of deuterium, catalyst

1. Introduction

The triple point of equilibrium hydrogen (e-H₂) is one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90)¹, and the triple point of equilibrium deuterium (e-D₂), which is an isotope of hydrogen, is currently being investigated as a possible candidate for the replacement of the two fixed points (the hydrogen vapor pressure points) at 17.0 K and 20.3 K in the ITS-90².

Molecular hydrogen and deuterium occur in two modifications, ortho and para, which differ in the nuclear spin arrangement. The fraction in each modification is a function of the temperature but the equilibration is only slowly established for both hydrogen and deuterium³⁻⁵. Since their triple point temperatures are dependent on the composition, a catalyst is required to establish the equilibrium before accurate measurements of each triple point.

Recently, it has been confirmed using open cells that there is a problem associated with the catalyst for e-H₂; large anomalous increases, which are caused by the interaction between hydrogen and the catalyst, exist in the heat capacity at temperatures just below the triple point, and the anomaly disturbs the measurements of the triple point of e-H₂³⁻⁴. On the other hand, although there has been much work on the measurements of the triple point of e-D₂ over recent years²⁻⁵⁻⁷, it has not been confirmed whether an anomaly caused by the interaction between deuterium and the catalyst exists or not in the heat capacity of e-D₂.

In the present study, the triple points of e-H₂ and e-D₂ have been examined using sealed cells and a calorimetric method. The sealed cells of e-H₂ and of e-D₂ were fabricated at National Metrology Institute of Japan (NMIJ) and at Istituto di Metrologia G. Colonnetti (IMGC), respectively. It is confirmed by precise calorimetric measurements that there is a large anomaly at temperatures just below the triple point in the heat capacity of e-H₂ cells including ferric hydroxide as a catalyst, as reported by the measurements of open cells⁶. It is also found the strong correlation between the amount of catalyst and the size of the anomaly. A similar anomaly is also discovered in the heat capacity of e-D₂ cell including gadolinium oxide as a catalyst at temperatures just below the triple point.

Fig. 1 Sealed cell fabricated at NMIJ⁸
2. Experimental

Fig. 1 shows the cell of e-H₂, which was designed at NMIJ; its inner volume is about 35 cm³ and a confined space for liquid and/or solid sample is about 2 cm³. In sealing cells, a metal O-ring is tightly held in place by a copper plug and a small stainless steel locking bolt using a filling system originally designed at NMIJ. On the contrary, the sample gas is possible to be simply replaced by releasing the locking bolt. The more general and detailed design of the cell including a gas filling system and technique of other gas samples than hydrogen will be described elsewhere⁹).

We made two fixed point cells, NMIJ H-1 and NMIJ H-2, for realization of the triple point of e-H₂. The cells contain 0.5 g and 0.12 g of ferric hydroxide as a catalyst for the ortho-para conversion of molecular hydrogen modifications, respectively. About 85 mmol of hydrogen are sealed in each cell. The nominal purity of the hydrogen source is better than 99.99999%. The cell of e-D₂ fabricated at IMGC includes about 45 mmol of deuterium and 0.25 g gadolinium oxide as a catalyst for the ortho-para modifications of molecular deuterium⁹).

The triple points of e-H₂ and e-D₂ have been realized calorimetrically using a two stage GM refrigerator. Fig. 2 shows a schematic side view of the adiabatic calorimeter for the realization of those triple points. The design of the system and the measuring procedure are based on those reported by Sakurai³,⁴). A fixed point cell is enclosed in an adiabatically controlled aluminum shield and is suspended from the ceiling of the adiabatic shield by cotton threads. The adiabatic shield is completely covered with oxygen free high conductivity copper radiation shields fixed to the two cooling stages of the refrigerator.

Two small ceramic encapsulated rhodium-iron (RhFe) thermometers, which have nearly the same temperature characteristics, were used to control the temperature of the adiabatic shield; one attached on the adiabatic shield and the other attached on the cell (Fig. 2). The temperature difference between the adiabatic shield and the cell was detected as a resistance ratio of the two RhFe thermometers. The ratio value, the deviation from which was input to a PID controller as a signal to control the temperatures of the adiabatic shield, was adjusted to make spurious heat flux minimized. Fig. 3 shows an example of the temperature drift of a fixed point cell near 14 K during adiabatic controlling. The temperature drift was suppressed within about 0.3 mK per hour.

Heat amount for calorimetry was calculated from the electric power given to the heater wound around cell and the period of heating. Usually, the manganin heaters of about 200 Ω and the heating currents of about 5 mA were used. The heating period was adjusted from a few minutes to about 15 minutes. At the triple point, less than 10 % of sample was melted by each heat pulse. A RhFe thermometer was used for the measurements of the triple points of e-H₂ and e-D₂. Its resistance was measured by the automatic direct current comparator bridge (Measurements International 6010-B).

3. Results and discussion

3.1 Equilibrium Hydrogen

Fig. 4 shows the heat capacities of NMIJ H-1 and NMIJ H-2 at temperatures near the triple point. A large extra peak, other than
the divergence due to the triple point, is observed for NMIJ H-1 at temperatures just below the triple point. Hereafter, the peak is referred as an anomaly. For NMIJ H-2, the anomaly is also observed in the heat capacity at the same temperature as that for NMIJ H-1. Its size of the anomaly is, however, markedly suppressed.

Table 1 shows the total heat due to the anomaly \( Q_a \) estimated from the heat capacity for each of NMIJ H-1 and NMIJ H-2. The heat \( Q_a \) does not include contributions from the normal specific heat of the solid and the liquid hydrogen and that of the cell\(^8\). The amounts of the catalyst included in NMIJ H-1 and NMIJ H-2 are also shown in the table. It is noted from the table that both the size of \( Q_a \) and the amount of the catalyst for NMIJ H-1 are about 4 times larger than those for NMIJ H-2. This correlation strongly supports that the anomaly on heat capacity curves comes from the interaction between a catalyst and hydrogen, as reported previously\(^4\).

The melting curves for NMIJ H-1 and NMIJ H-2 are shown in Fig. 5. The melting curves have been measured several times over a period about two weeks following the initial cooling. The data obtained in each run of the heat capacity measurement are plotted against the inverse of the melted fraction, \( 1/F \). From Fig. 5, the melting curves are found to agree with each other. This indicates that the spin equilibration was complete.

As seen in Fig. 5, the melting curves for NMIJ H-1 markedly deviate downward from those for NMIJ H-2 with increasing \( 1/F \); the melting range is over 1 mK. In contrast, the melting curves for NMIJ H-2 show linear dependence on \( 1/F \) within experimental error; the melting range is less than 0.05 mK. This means that the measurement results of the triple point for NMIJ H-2 are more reliable\(^9\).

The behavior of the melting curves for NMIJ H-1 is very similar to that of the melting curves for "e-H\(_2\)" cells including a large amount of a catalyst\(^3,4,10,11\); the melting curves of "e-H\(_2\)" are disturbed by the depression of the melting temperature due to the interaction between hydrogen and the catalyst. In fact, the large anomaly due to the interaction between the catalyst and hydrogen exists in the heat capacity for NMIJ H-1.

On the other hand, the anomaly of the heat capacity is markedly suppressed for NMIJ H-2, in which the amount of the catalyst was reduced. The reduction of the amount of the catalyst will cause the significant change of the melting curves from NMIJ H-1 to NMIJ H-2. This is consistent with the previous report\(^6,10,11\); the reduction of the amount of the catalyst will suppress the influence of the interaction between the catalyst and hydrogen.
3.2 Equilibrium Deuterium

Fig. 6 shows the heat capacity of equilibrium deuterium (e-D₂) measured using the sealed cell (S/N 5e-D₂-2000/03/24) fabricated at IMGC. It is noted that there is a large anomaly at temperatures just below the triple point on the heat capacity curves. This apparently indicates that there is an interaction between deuterium and the catalyst, which induces the anomaly on the heat capacity curves of e-D₂ in the same mechanism as e-H₂.

Fig. 7 shows the melting curves for 5e-D₂-2000/03/24. It is noted in Fig. 7 that the melting curves are markedly distorted and the melting range spreads over 4 mK. Since the large anomaly is observed in the heat capacity for 5e-D₂-2000/03/24, this disturbance of the melting curves will be caused by the interaction between deuterium and the catalyst, as observed for e-H₂.

4. Conclusion

By using the new designed sealed cells, we have realized the triple points of equilibrium hydrogen and equilibrium deuterium.

On the heat capacity curves for both equilibrium hydrogen and equilibrium deuterium, a large anomalous peak is observed at temperatures just below the triple point. The anomalous peak comes from an interaction between substances and a catalyst employed for the ortho-para equilibration.

In the case of the triple point of equilibrium hydrogen, it is confirmed that the reduction of the amount of the catalyst markedly suppresses this interaction and enables to obtain more reliable melting curves of the triple point of equilibrium hydrogen, as reported previously.

It is also expected for equilibrium deuterium that a reduction of the amount of the catalyst will suppress the influence of the interaction between the catalyst and deuterium and allow one to obtain more reliable melting curves of the triple point. It needs more studies on the triple point temperature of equilibrium deuterium by reducing the amount of the catalyst to realize the triple point of equilibrium deuterium at the highest level accuracy.

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