

T. Nakano¹, O. Tamura¹, H. Sakurai¹¹ National Metrology Institute of Japan, AIST Central 3, Tsukuba 305-8563, Ibaraki, Japan
tnt@ni.aist.go.jp

Abstract: The heat capacity of *e*-H₂ with powder of FeO(OH) used as a catalyst for ortho-para equilibration has been investigated using sealed cells fabricated at the National Metrology Institute of Japan. An anomalous double peak has been observed in their heat capacities at temperatures just below the triple point. Supercooling behavior has been observed not only at the triple point but also at each anomalous peak resulting from a depression of the melting temperature of a portion of solid H₂ in close physical proximity to the catalyst. The reduction of the amount of catalyst suppresses the size of the anomalies and allows one to obtain more reliable melting curves for *e*-H₂ at the triple point.

Keywords: catalyst; FeO(OH); hydrogen; ITS-90; triple point

1. Introduction

The triple point of equilibrium hydrogen (*e*-H₂) at 13.8033 K is one of the defining fixed points of the International Temperature Scale 1990 (ITS-90) and is used to calibrate standard platinum resistance thermometers and interpolation gas thermometers [1]. The triple-point temperature of H₂ depends on the composition of two isomers of molecular hydrogen (H₂), ortho- and para-H₂, which differ in nuclear spin arrangement [2-4]. A large amount of powder of a catalyst (such as ferric oxy-hydroxide, FeO(OH)) is traditionally used to establish the equilibrium concentration of the two isomers. This is because the equilibration is only slowly accomplished without the catalyst by changing temperature.

However, it has been recently confirmed that there is a problem for the triple point of *e*-H₂ when a large amount of powder of FeO(OH) is used as the catalyst; a large anomalous increase exists in the heat capacity at temperatures just below the triple point [2, 5-8], and the anomalies markedly influence the shape of the melting plateau and the triple-point temperature [5-10]. Furthermore, a recent report showed an anomalous double peak in the heat capacity just below the triple point, but the reduction of the amount of FeO(OH) suppresses the anomalies and makes the double-peak behavior unclear [8]. Clarification of the detailed behavior of the anomalies in the heat capacity has been expected to give a clue to understand its origin and one of the best ways to realize the triple-point temperature of *e*-H₂ at highest-level accuracy.

In this study, the heat capacity of *e*-H₂ with powder of FeO(OH) used as the catalyst was examined at temperatures around the triple point using sealed cells fabricated at the National Metrology Institute of Japan (NMIJ). The anomalous double peak has been evidently observed even when the cell included a small amount of FeO(OH). We also tried to check the detailed behavior of the double peak in the heat capacity using, and confirmed that the double peak occurs in the heat capacity independent of the amount of FeO(OH). Supercooling behavior characteristic of a first order phase transition also appears not only at the triple point but also at each anomalous peak, implying that the anomalous peaks could be caused by two or three coexisting parts within the solid H₂. The part of the solid in close physical proximity to the catalyst appears to have a lower melting temperature due to an interaction between the powder of FeO(OH) and that portion of solid H₂.

2. Experimental

The detailed designs of cells of NMIJ including gas filling systems and related techniques have been described in Refs. [8, 9]. In this study, we used three NMIJ cells, H-1, H-2, and H-5. The nominal chemical purity by volume of H₂ source is better than 99.999 99 %. The cell was filled up to about 7 MPa of hydrogen at room temperature. So, each cell was filled with about 85 mmol of hydrogen from the same source. The cells contain 0.5 g, 0.12 g and 0.015 g of ferric oxy-hydroxide as the catalyst, respectively.

Measurements of the heat capacity around the triple point for the *e*-H₂ sealed cells have been carried out with the adiabatic calorimeters. These apparatus and the detailed measurement procedures have been reported elsewhere [8, 9].

3. Results and discussion

3.1 Heat Capacity of *e*-H₂ with FeO(OH)

Figure 1 shows the heat capacities of *e*-H₂ cells (H-1, H-2, and H-5) near the triple point. An anomalous double extra peak, other than a divergence due to the triple point, is evidently observed for these cells at temperatures just below the triple point. Hereafter, each peak is referred to as an anomaly. The first anomaly, which is nearer to the triple point, is much larger than the second one. The anomalies are suppressed in magnitude by reducing the amount of the catalyst, as seen in Fig 1.

In the former report [8], the existence of second anomalies for cells H-2 and H-5 was unclear. But, the second anomaly can be clearly observed, even for cell H-5 including only 0.015 g of FeO(OH) by reducing the size of each heat pulse down to 0.005 J in the present study, as seen in the inset of Fig. 1. Tew also observed a similar anomalous double peak using a sealed cell fabricated at the National Institute of Standards and Technology (NIST) [11]. Recently, Fellmuth, *et. al.* [12] also confirmed the anomalous double peak in the heat capacity of *e*-H₂. These results indicate that the double peak-behavior in the heat capacity of *e*-H₂ with powder of FeO(OH) is a universal property independent of H₂ sources, FeO(OH) sources, and sealed-cell designs.

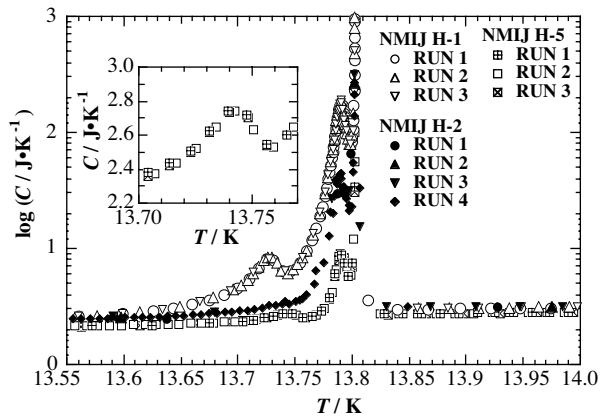


Fig. 1. Heat capacities near the triple point observed by using: H-1, H-2 and H-5 cells fabricated at NMIJ. The inset is an enlarged figure of the heat capacity of H-5 near the second anomaly [11].

Figure 2 shows the enthalpy gain due to the anomalies and the triple-point transition of cell H-1 obtained from integration of the excess of heat capacity over the normal heat capacity in the same way reported in Ref. 8. The inset of Fig. 2 shows the dependence on the amount of FeO(OH) of the enthalpy gain due to the triple-point transition (ΔH_0), first anomaly (ΔH_1), and second anomaly (ΔH_2). The sizes of ΔH_1 and ΔH_2 increase in proportion to the amount of the catalyst. This correlation strongly indicates that the catalyst causes both heat capacity anomalies.

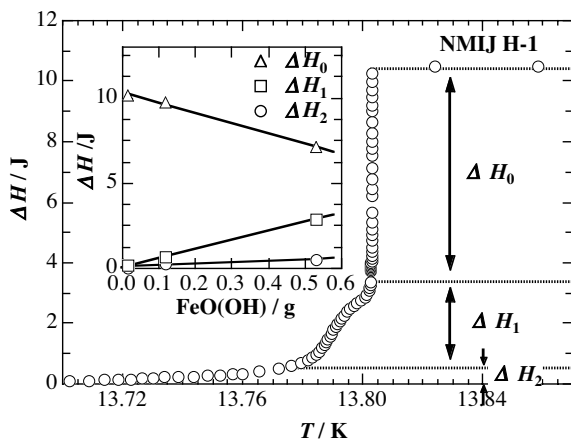


Fig. 2. Enthalpy gain due to the anomalies and the triple-point transition of cell H-1 obtained from integration of the excess of heat capacity over the normal heat capacity. The inset shows the dependence on the amount of catalyst of the enthalpy gains due to the triple-point transition (ΔH_0), first anomaly (ΔH_1), and second anomaly (ΔH_2) [11].

The total enthalpy gain due to both of the anomalies and the triple-point transition, $\Delta H_0 + \Delta H_1 + \Delta H_2$, is about 10 J and is consistent with the total heat of fusion expected from the amount of H₂ in each cell, as reported in Ref. 8. This strongly

suggests that the anomalous double peak is related to the melting of a portion of the solid H₂.

Figure 3 shows the freezing curve of H₂ observed using cell H-1. The cooling power was about 20 mW. First, the temperature decreases to about 30 mK below the triple-point temperature because of supercooling. Next, the temperature jumps up to the triple-point temperature and stabilizes for about 9 hours because of solidification of H₂ at the triple point. Later, the temperature starts to decrease and shows a “shoulder” behavior around temperatures where the anomalies in the heat capacity have been observed. As seen in the inset of Fig. 3, there is a small peak in temperature around the shoulder. Finally, the temperature decreases steeply.

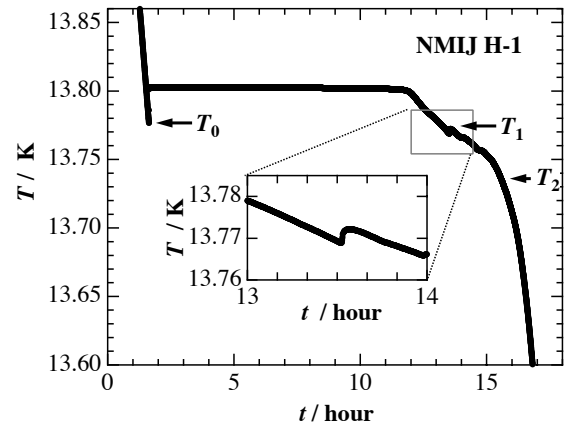


Fig. 3. Freezing curve observed by using cell H-1. The inset is an enlarged figure of the freezing curve near the shoulder behavior [11].

To check the heat capacity in the supercooling state, adiabatic calorimetry was started around the temperature T_0 in Fig. 3. To investigate the origin of the shoulder behavior, we also stopped the cooling at temperatures around the shoulder, T_1 and T_2 in Fig. 3, and then started measurements of heat capacity for cell H-1.

Figure 4 shows the heat capacity of cell H-1, measurements of which were started at temperatures T_0 , T_1 , and T_2 in Fig. 3. The heat capacity of run T_0 , namely the heat capacity in the supercooled state, shows almost a constant behavior around the triple point without any anomaly at those temperatures, where the first anomaly was observed. This means that the anomalies will not occur without solid H₂. It is consistent with the above suggestion that the anomalies are related to the melting of a portion of the solid H₂.

As seen in Fig. 4, the heat capacity of run T_1 increases with increasing temperature without showing the first anomaly and agrees with the divergent part of the heat capacity due to the triple point at higher temperatures. This strongly suggests that the supercooling of the first anomaly phase will occur independently of the normal transition at the triple point. Similar behavior was also observed in run T_2 at temperatures around the second anomaly, as seen in the inset of Fig. 4. These results imply that the solid H₂ is segregated into three parts with three different melting temperatures. The shoulder

behavior in Fig. 3 will be caused by the solidification of parts of H₂ with lower melting (freezing) temperatures.

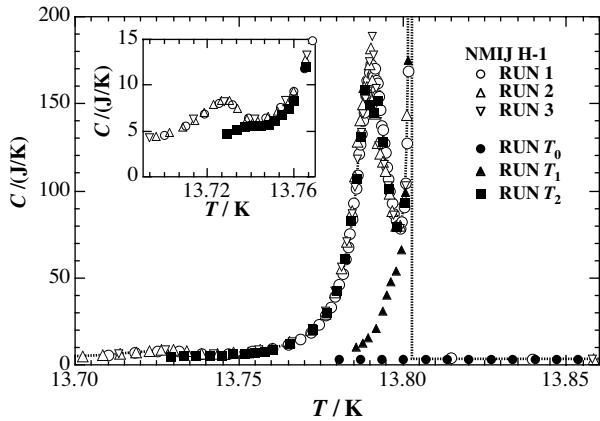


Fig. 4. Heat capacity of cell H-1, measurements that were started at temperatures T_0 , T_1 , and T_2 in Fig. 4 [11].

Figure 5 shows a schematic view of solid H₂ with FeO(OH) filled in a cell. The presence of the catalyst particles naturally segregates the solid H₂ into two volumes within the cell; one volume contains the solid H₂ coexisting with the catalyst FeO(OH), and the other volume contains the solid H₂ separated from the catalyst. As mentioned above, the size of anomalies in the heat capacity curves shows a linear dependence on the amount of the catalyst [8, 9]. So, the anomalies will come from the solid H₂ coexisting with the catalyst.

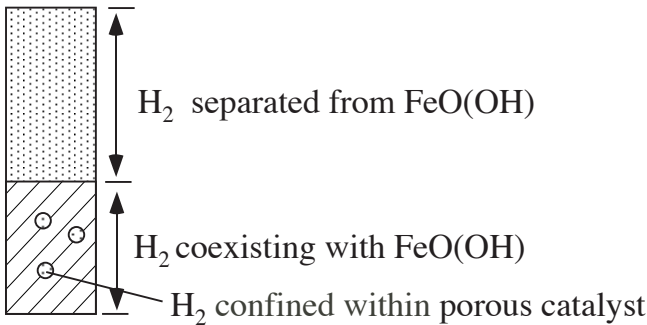


Fig. 5. Schematic view of solid H₂ with FeO(OH) filled in a cell [11].

As seen in Fig. 6, a porous structure is observed in powder of FeO(OH) by using a scanning electron microscope [14]. A lot of small whiskers of FeO(OH) are gathered and there are a lot of gaps among the whiskers. The gap size, namely size of pores, seems to be the order of magnitude of 100 nm. Probably, a part of H₂ confined within such pores of catalyst (Fig. 5) will be followed by a depression of the melting temperature.

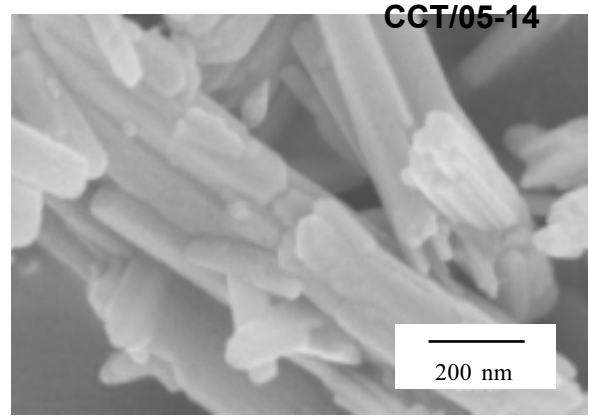


Fig. 6. SEM images of FeO(OH) [14].

Similar phenomena have been actually observed for H₂ in porous Vycor glass [15, 16]. A shoulder behavior was observed in the freezing curve of H₂ in the Vycor pores below the triple-point temperature separate from a normal freezing plateau [16]. It was also reported that a large peak appears on the heat capacity curves of H₂ in porous Vycor glass below the normal triple-point temperature of H₂ because of the depression of the melting temperature of H₂ in restricted geometries [15].

If the melting temperature of a portion of hydrogen is suppressed by the confinement of the hydrogen in a restricted geometry, namely pores of the catalyst, the size of the suppression will be proportional to the inverse of radius of the catalyst pores, inferred from the results for hydrogen confined within the Vycor porous glass. It is estimated that the order of magnitude of radius of the catalyst pores will be 100 nm because the order of the depression of the melting temperature of the portion of hydrogen is about 10 mK for our result. Actually, the order of magnitude of radius of the pores of our catalyst FeO(OH) observed in the SEM image is consistent to the above estimation. This supports that the anomaly of the heat capacity, namely, the suppression of the melting temperature of a portion of hydrogen will be mainly caused by the confinement of the portion of hydrogen within pores of the catalyst.

The reason for the appearance of the double peak is not clear from this study alone, but it may come from the existence of two intrinsic pore radii in the porous catalyst. Actually, a double peak was observed owing to the existence of two distinct pore radii in the pore-size distribution of Vycor glass [16]. Or it may be possible that the second (lower temperature) anomaly is caused by a solid-solid transition for that portion of the H₂ within the pores of the catalyst particles [11].

3.2 Melting Curves of e-H₂ at the Triple Point

The melting curves for H-1, H-2, and H-5 cells are shown in Fig. 7. The data obtained in heat capacity measurements are plotted against the inverse of the melted fraction, 1/F. To evaluate F , ΔH_0 was used as the total heat of fusion. In Fig. 7, the melting curves reported in Ref. 8 are also shown. In Ref. 8, the melted fraction F was evaluated by using $\Delta H_0 + \Delta H_1 + \Delta H_2$ as the total heat of fusion; that is, the melting curves reported

in Ref. 8 included the contribution of a portion of solid H_2 with lower melting temperatures due to the influence of the catalyst.

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References

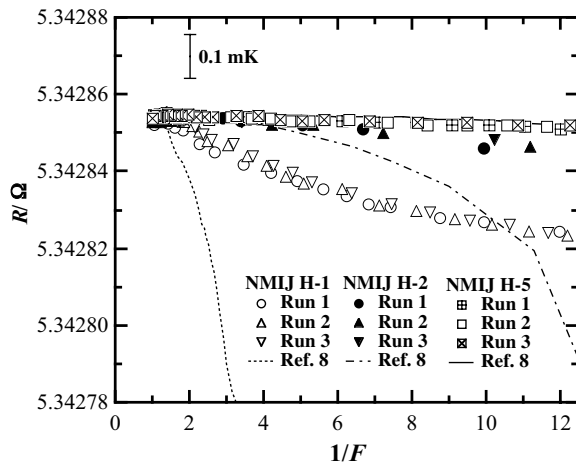


Fig. 7. Melting curves obtained by using cells H-1, H-2, and H-5. Dashed, dashed-dotted, and solid lines are melting curves reported in Ref. 8 for cells H-1, H-2, and H-5, respectively.

As seen in Fig. 7, the widths of the melting curves of cells H-1 and H-2 become narrow within about 0.2 mK in the wide region of $1/F$ up to $1/F = 12$ by removing the contribution of ΔH_1 and ΔH_2 . On the other hand, both melting curves for H-5 obtained in the present study and in Ref. 8 show the same linear dependence on $1/F$. This is because the contributions of ΔH_1 and ΔH_2 for cell H-5 are very small as a result of the reduction of the amount of the catalyst.

The melting curve of cells H-1 show almost the same value as cell H-5 at $1/F < 2$, but they deviate downward from the linear dependence of cell H-5 with increasing $1/F$ for $1/F > 2$ even though the contributions of ΔH_1 and ΔH_2 were removed. Probably, this suggests that the influence of the catalyst causing the suppression of the melting temperature will reach outside of the catalyst when a large amount of the catalyst was used.

CONCLUSION

The heat capacity of e- H_2 with powder of FeO(OH) used as the catalyst for ortho-para equilibration has been examined using sealed cells fabricated at the National Metrology Institute of Japan (NMIJ). An anomalous double peak appears in their heat capacities at temperatures just below the triple point. The position of the double peak is fairly insensitive to the amount of catalyst. The supercooling behavior has been observed not only at the triple point but also at each anomalous peak, implying that the anomalous double peak will be caused by the depression of the melting temperature in restricted geometries or other endothermic transformations of the solid H_2 due to interactions between the catalyst and H_2 . A reduction of the amount of catalyst suppresses the influence of the catalyst and allows one to obtain more reliable melting curves for e- H_2 .

1. H. Preston-Thomas, *Metrologia* **27**: 3 (1990), *ibid.*: 107 (erratum).
2. H. Sakurai, *T. SICE*, **34**: 1153 (1998).
3. *Supplementary Information for the International Temperature Scale of 1990*, BIPM, (1990).
4. F. Pavese and G. Molinar, *Modern Gas-Based Temperature and Pressure Measurements* (Plenum Press, New York, 1992) sub-section 2. 3. 2. 3.
5. H. Sakurai, in *Proceedings of TEMPMEKO 2001*, B. Fellmuth, J. Siedel, and G. Scholz, ed. (VDE Verlag GmbH Berlin, 2002), pp. 411-416.
6. H. Sakurai, in: *Temperature, its Measurement and Control in Science and Industry*, Vol. 7, D. C. Ripple, ed. (American Institute of Physics, Melville, New York, 2003), pp. 969-974.
7. B. Fellmuth, D. Head, F. Pavese, A. Szmyrka-Grzebyk, W. Tew, in *Proceedings of TEMPMEKO 2001*, B. Fellmuth, J. Siedel, and G. Scholz, ed. (VDE Verlag GmbH Berlin, 2002), pp. 403-405.
8. T. Nakano, O. Tamura and H. Sakurai, in: *Temperature, its Measurement and Control in Science and Industry*, Vol. 7, D. C. Ripple, ed. (American Institute of Physics, Melville, New York), pp.185-190, (2003).
9. T. Nakano, O. Tamura and H. Sakurai, *T. SICE* **38**: 947 (2002).
10. A. G. Steele, in *Proceedings of TEMPMEKO 2001*, B. Fellmuth, J. Siedel, and G. Scholz, ed. (VDE Verlag GmbH Berlin, 2002), pp. 417-422.
11. T. Nakano, W. L. Tew, O. Tamura and H. Sakurai, *International Journal of Thermophysics* **26**, 84 (2005).
12. B. Fellmuth, L. Wolber, Y. Hermier, F. Pavese, P.P.M. Steur, I. Peroni, A. Szmyrka-Grzebyk, L. Lipinski, W.L. Tew, T. Nakano, H. Sakurai, O. Tamura, D. Head, K.D. Hill, A.G. Steele, *Metrologia* **42**, 171 (2005).
13. P. L. Barrick, L. F. Brown, H. L. Hutchinson, and R. L. Cruse, *Adv. Cryo. Eng.*, **10A**: 181 (1965).
14. T. Nakano, O. Tamura and H. Sakurai, submitted to *Proceedings of TEMPMEKO 2004*, June 22-25, 2004, Croatia.
15. J. L. Tell and H. J. Maris, *Phys. Rev. B* **28**: 5122 (1983).
16. R. H. Torii, H. J. Maris, and G. M. Seidel, *Phys. Rev. B* **41**: 7167 (1990).