

On the triple point of equilibrium hydrogen

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The heat capacity of solid and liquid equilibrium hydrogen and its triple point are calorimetrically studied by an open cell system using a closed cycle refrigerator. Different shapes of the heat capacity curves of solid hydrogen are observed at temperatures near the triple point in the case of about 2 g of ferric hydroxide as a catalyst for the ortho-para equilibration against about 0.1 mol of hydrogen and in the case of about 0.2 g of the catalyst. In the latter case, the melting curves of the triple point are calorimetrically measured using three different sources of hydrogen and the large sample dependency of the triple point temperature of equilibrium hydrogen is observed. The maximum difference among three samples is about 0.338 mK, which may be caused by the isotopic variation of natural hydrogen. The results of the mass analysis show that the dependence of the triple point temperature is 0.005 mK per ppm of deuterium in the hydrogen.

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1 Heat capacity anomaly of solid and liquid hydrogen

The heat capacities of hydrogen, excluding the fixed point cell, at temperatures near the triple point were measured using 2 g of ferric hydroxide as a catalyst for ortho-para conversion of about 0.1 mol of hydrogen. The results are shown in Fig.1. They are nearly the same as those reported for a sealed cell²⁾. An extra peak, other than the triple point, with the increase of the heat capacity of solid hydrogen at temperatures just below the triple point was observed, which is not a normal shape of heat capacity curve near the triple point. The peak temperature is nearer to the triple point than the case in the sealed cell.

This anomaly differs from the premelting of the triple point. As shown later, the heat capacity is also increased by the premelting of the triple point, but the catalyst anomaly is much larger and indicates stronger interaction between sample hydrogen and the catalyst.

From the results, it may be that a catalyst shows the anomaly on heat capacity curves at temperatures around the triple point when a large amount of a catalyst is used compared with the amount of the sample. For the realization of the thermometric fixed points, a situation where

there is an anomaly in the heat capacity at temperatures near the fixed point is generally unsatisfactory, and the anomaly probably affects the fixed point temperatures. The melting curves of the triple point were deformed compared with the results described below with a small amount of a catalysts.

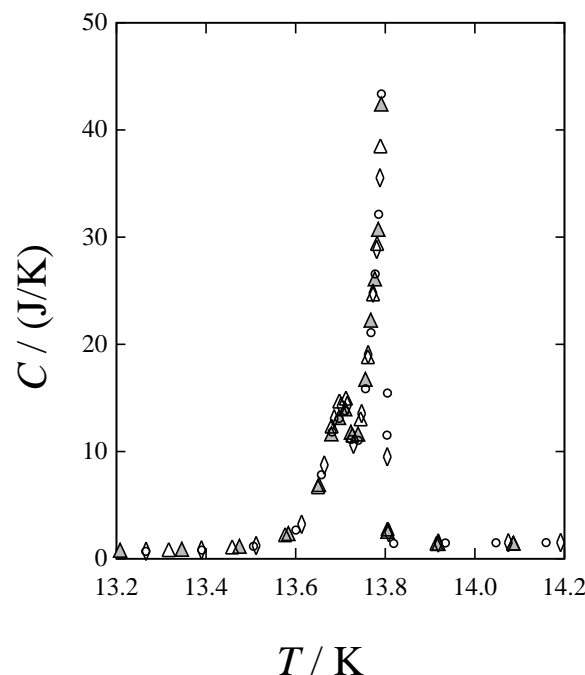


Fig. 1: Heat capacity of hydrogen in the case of 2 g of a catalyst at temperatures near the triple point.

^{*)}written by L^AT_EX2_ε on FreeBSD.

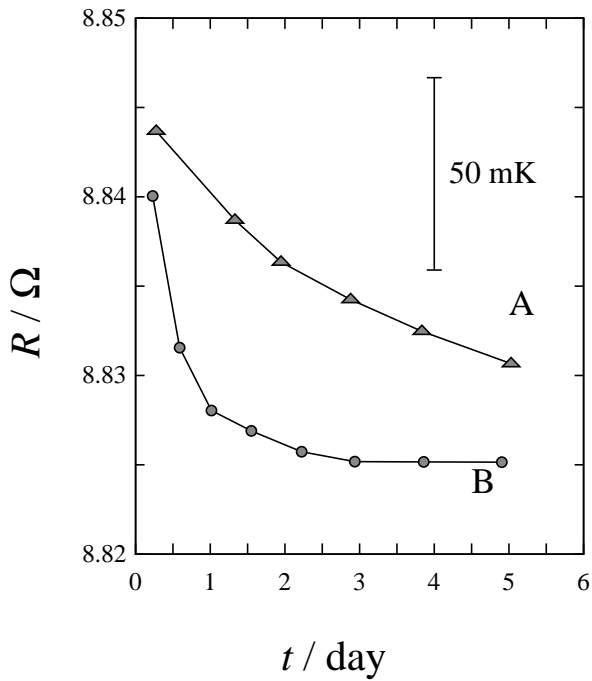


Fig. 2: An example of changes of the triple point temperatures with time by ortho-para conversion in the case of less than 0.2 g (A) or about 0.2 g (B) of ferric hydroxide as a catalyst

2 Equilibration of ortho-para hydrogen

The shape of the heat capacity curve of solid hydrogen depended on the amount of a catalyst and the anomaly became negligible in the case of the order of 0.1 g of a catalyst. But as has been already pointed out³⁾, the conversion rate became small and it took more than a week to complete the ortho-para equilibration. It was found that a mass of catalyst of about 0.2 g against about 0.1 mol of hydrogen gave no detectable anomaly on the heat capacity curve and an acceptable period for equilibration, i.e. a few days.

In this experiment the equilibration of ortho- and para-hydrogen was confirmed by measuring the changes of the triple point temperatures as shown in **Fig.2**. The data indicated by 'B' in this figure are the results in the case of about 0.2 g of ferric hydroxide as catalyst. The triple point temperatures became constant within the experimental errors of 0.1 mK after 3 days.

But in the case of less than 0.2 g, the orth-para conver-

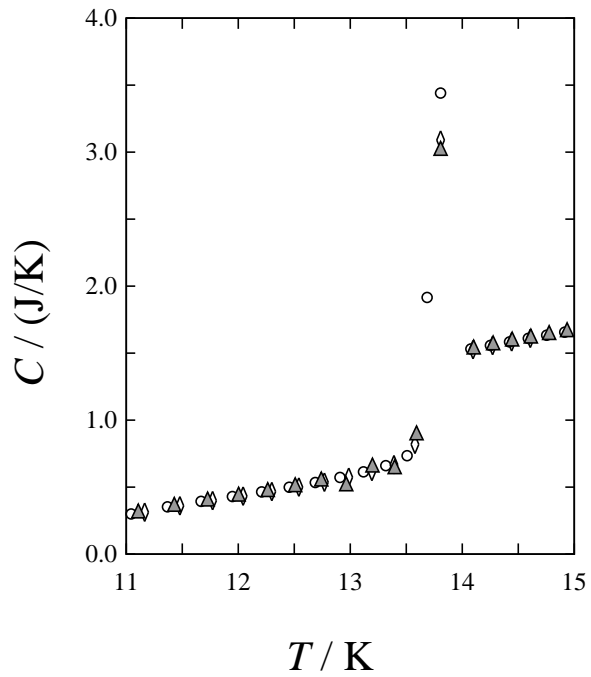


Fig. 3: Heat capacity of solid and liquid hydrogen at temperatures near the triple point in the case of about 0.2 g of ferric hydroxide.

sion period became longer as shown in the curve 'A' in **Fig.2**. In this case the mass of catalyst is less than 0.2 g but larger than 0.1 g. As the measurement of the mass of ferric hydroxide below 0.2 g is not so easy, it is difficult to clarify the critical amount of the catalyst. But the value of around 0.2 g may be optimal for obtaining equilibrium hydrogen while also eliminating the thermal anomaly.

In the case of about 0.2 g of catalysts in about 0.1 mol of hydrogen, no anomaly was observed on the heat capacity curve of solid hydrogen, as shown in **Fig.3**. The pre-melting heat capacity increase is also clearly observed at temperatures just below the triple point. But this increase is more than ten times smaller than the catalyst anomaly. In the case of less than 0.2g of a catalyst, such as the case of 'A' in **Fig.2**, there was also no anomaly on the heat capacity. From these results, such a small amount of the catalyst may have a smaller effect on the triple point temperature than that of the recommended realization¹⁾.

3 Sample dependency of the triple point temperature

Hydrogen molecule is a mixture of H_2 , HD and D_2 . On average natural hydrogen is said to contain about 0.015% of deuterium. But the ratio of D to H depends largely on the source of hydrogen⁴⁾. The sample dependency of the triple point temperature of hydrogen was estimated experimentally using three different sources of hydrogen. About 0.2 g of ferric hydroxide as catalyst in 0.1 mol of hydrogen were used in this experiment. The results are shown in Fig.4. The data were obtained in several runs of heat capacity measurement after equilibration and were plotted against the inverse of the melted fraction $1/F$. Almost all the data show linear dependence on $1/F$ within experimental error. But three samples show a systematic difference in the triple point temperature. The maximum difference among these samples is about 0.338 mK at the extrapolated value of $1/F=0$.

The deuterium content of two samples was determined by a mass analysis. Sample A contains about 33 ppm of deuterium and Sample C has about 101 ppm. From these data, the deuterium dependency of the triple point of equilibrium hydrogen is about 0.005 mK per ppm of deuterium. This value was estimated from the temperature when the inverse of the melted fraction is extrapolated to zero. So it may be about 10 % larger than that of the value at the melted fraction of 1.

This value includes such uncertainties as follows.

1. In this experiment, an open cell was used and it took about 3 h to liquefy the sample hydrogen into the fixed point cell. There is no guarantee that the deuterium content of the sample in the container at room temperature is kept in the cell.
2. In the cell, filling tube and ferric hydroxide, there are hydrogen molecules or ions. So there is a possibility that the deuterium in the sample gas was replaced by such hydrogen.

But by estimating from other catalyst experiments, the corrections from these items may be small.

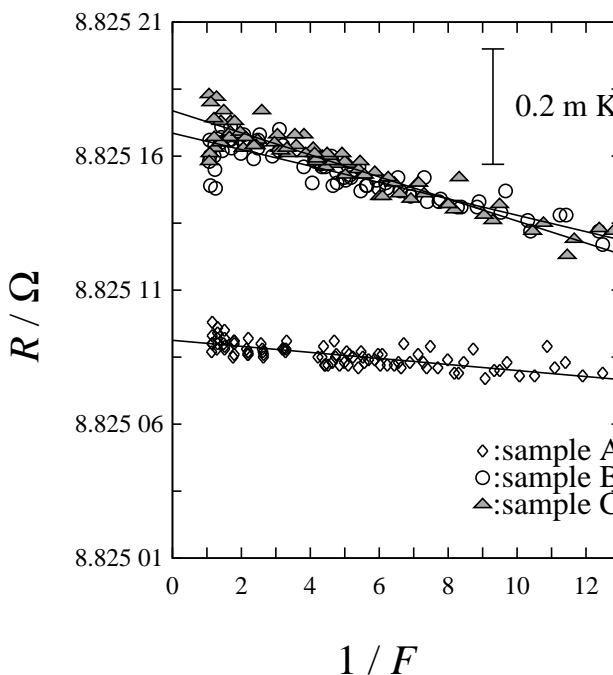


Fig. 4: Sample dependency of the triple points of equilibrium hydrogen.

4 Conclusion

The anomaly in the heat capacity of solid and liquid hydrogen is caused by the interaction between hydrogen and the catalyst employed to equilibrate ortho-para hydrogen. To reduce the anomaly, one needs to use an amount of a catalyst that is small compared with the amount of sample hydrogen. In this case, a number of days are required to equilibrate ortho-para hydrogen.

The isotopic dependency of the triple point of equilibrium hydrogen is estimated to be about 0.005 mK per ppm of deuterium.

References

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