Influence of the Heat Capacity Anomaly on the Triple Point Temperature of Equilbrium Hydrogen

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Abstract: The relation between the melting curves of equilibrium hydrogen and a catalyst of Gd_2O_3 for ortho-para conversion of hydrogen is systematically studied. It is confirmed that hydrogen in the cell is spatially separated into two parts, i.e. hydrogen interacting with the catalyst and the rest of hydrogen. The interacting hydrogen with the catalyst shows another melting curve of hydrogen. Approximately two parts of hydrogen melt independently. The main melting curve of equilibrium hydrogen seems to be influenced little by the catalyst.

1. Introduction

It was pointed out that the heat capacity does anomalously increase at temperatures just below the triple point of equilibrium hydrogen when using a catalyst for the equilibration of ortho- and para-hydrogen[1, 3, 4, 5, 10] . The heat capacity anomaly distorts the pre-melting of the hydrogen triple point[6, 7] . Such anomalies or distortions are not suitable for the fixed point realization.

In this report some suggestions will be given from the measurement results of the correlation between the heat capacity anomaly and the amount of sample hydrogen using gadolinium oxide as a catalyst for ortho-para conversion of hydrogen.

2. Measurement

The measurement was done using an open cell with a small amount of Gd_2O_3 as a catalyst by an adiabatic calorimetric method. About 0.62 mmol of powder gadolinium oxide encapsulated by thin Japanese paper was placed at the bottom of the fixed point cell. The catalyst was localized only at some small part of the fixed point cell. The hydrogen of 12 mmol, 25 mmol, 40 mmol or 78 mmol was condensed in the cell. After equilibration of ortho- and para-hydrogen, the heat capacity of solid and liquid hydrogen was measured by an adiabatic calorimetric method. By changing the amount of hydrogen, the characteristics of the heat capacity and melting curves were studied.

The measuring system including a cryostat was nearly the same as reported[8] .

3. Results and discussion

3.1 Heat capacity anomaly

As same as a catalyst of ferric oxy-hydroxide[1, 3, 8] , an anomalous heat capacity increase caused by the catalyst of gadolinium oxide was observed at temperatures just below the triple point. This heat capacity increase is referred as a heat capacity anomaly in this report. Some results of the heat capacity measurement at different amount of hydrogen are shown in **Fig.1**. The anomalous peak in the heat capacity was observed at about 13.8 K, i.e., about 3 mK below the triple point, in the case of the present experimental situation. Its temperature may depend on the experimental situation. This figure shows that the shapes of the anomalous curves do not depend on the total amount of hydrogen in the cell.

> The second anomalous peak was not observed, except small increase of heat capacity at temperatures from about 13.7 K to the first anomalous peak. This increase is ignored in this report.

3.2 Interacting hydrogen

The heat capacity anomaly was systematically measured by changing the amount of hydrogen. The results are summarized in **Table 1**. In calculating the amount of hydrogen of the interaction hydrogen with the catalyst, we assumed that the latent heat of fusion of the hydrogen interacting with the catalyst is the same as that of non-interacting hydrogen. This table shows that the total latent heat of the anomaly, i.e. Q_A, does not depend sharply on the total amount of hydrogen. This means that the amount of hydrogen interacting with the catalyst is constant and is not disturbed by the rest of hydrogen in the cell.

From this table, it is possible to know how many molecules of hydrogen are interacting with a molar of the

Table 1: Relation between the anomalous hydrogen and the normal hydrogen in the case of gadolinium oxide

Total amount	Anomalous hydrogen		Normal hydrogen	
N_{T}/mmol	Q_{A}/J	N_{A}/mmol	Q_{N}/J	N_{N}/mmol
12	0.27	2.3	1.0	8.6
25	0.26	2.2	2.3	19.6
40	0.22	1.9	4.3	37.2
78	0.25	2.2	8.1	69.6
average	0.249	2.13		

Catalyst: Gd_2O_3, 0.62 mmol, N_{T}: total amount of liquefied sample, N_{C}: amount of the catalyst, Q_{A}:total heat at anomaly, N_{A}:amount of hydrogen calculated from Q_{A} divided by the heat of fusion, Q_{N}: total heat at normal parts, N_{N}: amount of hydrogen calculated from Q_{N} divided by the heat of fusion,

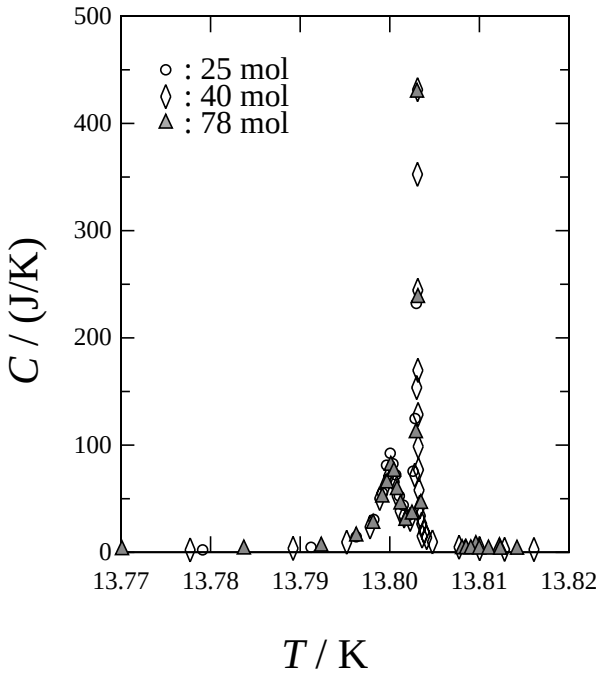

Fig. 1: The relation between the amount of hydrogen and anomalies in the heat capacity at temperatures near the triple point when using 0.62 mmol of gadolinium oxide.

catalyst from calculating the ratio between the amount of the interaction hydrogen and that of the catalyst, i.e. $N_{\mathrm{A}}/N_{\mathrm{C}}$. In the case of Gd_2O_3, the value is 3.42 mol/mol. This says that the amount of the interacting hydrogen with a molar catalyst is about 3.4 molecules. This value seems to be reasonable. Rigorously it may depend on the density and the kind of a catalyst.

3.3 Melting curves

The Table 1 is also giving important information.

1. The interacting hydrogen with the catalyst, which gives an anomaly in the heat capacity at temperatures just below the triple point, is nearly independent of the rest of hydrogen.
2. The sum of N_{A} and N_{N} is nearly equal to N_{T}.

N_{T}'s are estimated from the gas pressure in the container at room temperatures. The values are not so accurate, and are a little bit larger than the sum values. However, within this uncertainty it is reasonable to think that the heat capacity anomaly is caused by some phase transition between solid and liquid[4] . These are suggesting that there are two independent phase transitions, i.e. the melting of hydrogen which is interacting with the catalyst and that of the rest of hydrogen.

Based on this idea, the heat capacity data of Fig.1 were separated into two sets including a heat capacity peak, i.e. one with the anomalous peak and another with the normal triple point peak. Assuming both are independent, two melting curves can be calculated from each data set. The dividing temperature has some ambiguity as the two peaks are not completely separated, but in the case of gadolinium oxide in this experiment the anomalous curve is relatively sharp compared with those of ferric oxy-hydroxide[2, 10] . Further as the temperature of the heat capacity anomaly is close to the triple point temperature of equilibrium hydrogen, the dividing temperature is not so effective. The minimum point of the heat capacity curve is selected as the dividing temperature in this calculation. By this artificial division, the errors in heat are of the order of 0.1 J, which are not negligible for the anomalous part, but are negligible for the normal melting curves. So the uncertainty of the melting curve of the interacting hydrogen with the catalyst is suspected to

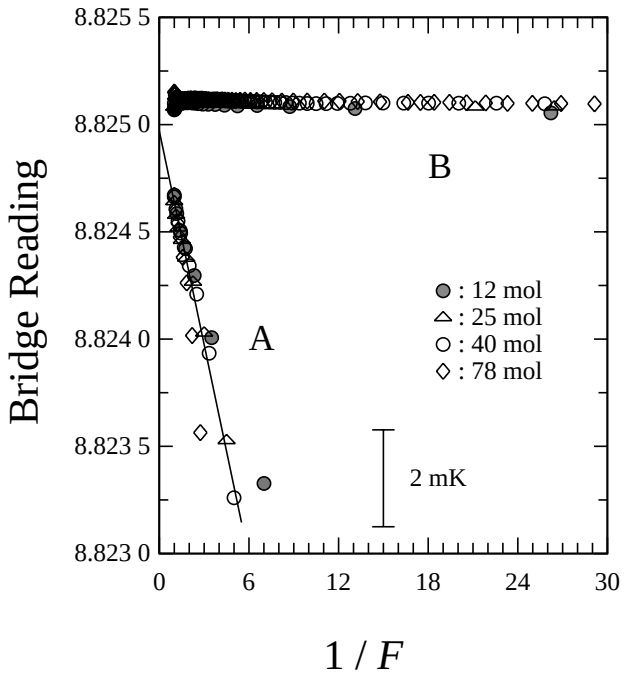

Fig. 2: Double melting curves of the hydrogen interacting with the catalyst (group A) and of the rest of hydrogen (group B). The solid line is estimated from the data of the group A.

become large compared with that of the normal melting curves.

Two melting curves calculated by this separation are shown in **Fig.2**, where F is the fraction of melt of each hydrogen. The lower temperature melting curves,(group A), are the melting curves of the interacting hydrogen and the higher,(group B), are those of the rest hydrogen. The curves of the group A do not depend on the total amount of hydrogen and agree with each other within the experimental and calculation uncertainties. On the other hand, the melting curves of the group B also agree with each other within the measurement uncertainties.

This figure is also showing another important fact. The curves of the group A have a relatively good linear relation between the resistance and $1/F$ in considering that the curves in the group A are suspected to have large uncertainties. The curves of the group A behave like the melting curves of hydrogen including a large amount of impurities. It needs further discussions whether the interacting hydrogen with the catalyst is equilibrium hydrogen or not. But the extrapolated value to $1/F = 0$ of the line of the group A is a good agreement with the value of the curves of B.

4. Conclusion

The hydrogen in the fixed point cell including the catalyst seems to be spatially separated into two independent virtual substances, which are not strongly correlated with each other. The melting curves of the interacting hydrogen with a catalyst are a large gradient and the catalyst behaves like impurities. The non-interacting hydrogen and the interacting hydrogen with the catalyst can melt independently, but small correlations may exist at the boundaries of two groups of hydrogen.

As an approximate conclusion, the anomalous heat capacity is simply indicating the phase transition between solid and liquid of the interacting hydrogen with the catalyst. Considering the case of *a small amount of the catalyst*, the anomaly may not influence the main melting curves of equilibrium hydrogen.

References

1 H. Sakurai, Trans. Soci. Instr. Contr. Engineers, 34 (1998) 1553-1558

2 H. Sakurai, Trnas. Soci. Instr. Contr. Engineers, 36 (1999) 734-748

3 H. Sakurai, Proceedings of Tempmeko99 (Van Schwinden Laboratorium, Delft 1999) 124-128

4 T. Nakano, O. Tamura and H. Sakurai: Trnas. Soci. Instr. Contr. Engineers, 38 (2002)947-951

5 T. Nakano, O. Tamura, H. Sakurai, Temperature, Its Measurement and Control in Science and Industry Vol.7 (to be published)

6 B. Fellumth, D. Berger, and L. Wolber: Proceedings of Tempmeko99 1999 (Van Schwinden Laboratorium, Delft 1999) 233-238

7 B. Fellumth, D. Head, F. Pavese, A. Szmyrka-Grzebyk and W. Tew: Proceedings of 8th Temperature Symposium on Temperature and Thermal Measurements in Industry and Science (VDE Verlag GMBH, Berlin 2001) 403-410

8 H. Sakurai, Proceedings of 8th Temperature Symposium on Temperature and Thermal Measurements in Industry and Science (VDE Verlag GMBH, Berlin 2001) 411-416

9 A. Steele, Proceedings of 8th Temperature Symposium on Temperature and Thermal Measurements in Industry and Science (VDE Verlag GMBH, Berlin 2001) 417-422

10 H. Sakurai: Temperature, Its Measurement and Control in Science and Industry Vol.7 (to be submitted)