**Physics.** — *"The specific heat at low temperatures. IV. Measurements of the specific heat of liquid hydrogen. Preliminary results on the specific heat of solid hydrogen and on the heat of fusion of hydrogen."* By W. H. KEESOM and H. KAMERLINGH ONNES. Communication N°. 153*a* from the Physical Laboratory at Leiden. (Communicated by H. KAMERLINGH ONNES).

(Communicated in the meeting of June 24, 1916).

§ 1. After the measurements of the specific heat of solid and liquid nitrogen (Comm. N°. 149*a* Jan. 1916) others were undertaken concerning liquid and solid hydrogen. The apparatus used were those described in Comm. N°. 149*a*.

In order to obtain a temperature as nearly as possible uniform in the experiments in which the calorimeter was surrounded by solid hydrogen, the calorimeter-vessel in the last three series of measurements was surrounded by a cylinder of copper which was closed at the top by tin-foil [1]). As the cryostat did not provide sufficient room for both the copper cylinder and the stirrer, the latter was removed in this case.

In the measurements of Oct. 23 (table II) and of Nov. 3 (table I), as it appeared afterwards, an error has crept in the measurement of the tension of the heating current at the terminals of the constantin wire of the central heating-core [2]). For these measurements, therefore, the number of Joules supplied was calculated from the current and the resistance of the heating-wire. This resistance which includes that of the platinum supply-wires which reach outside the calorimeter-vessel is a little different according to the vacuum in

[1]) Cf. p. 1004 note 1.

[2]) For the purpose of accurate measurements of the specific heat of metals and alloys (e.g. of nickel and copper in connection with the magnetic properties of these alloys, comp. Suppl. No 36 c, May 1914, p. 110 note 1) a new heating-core has been constructed in which the thermometer wire is suspended freely in a gas filled space in order to get rid of the changes to which the thermometer-wire is subject when it lies enclosed in enamel-paint.

the calorimeter-vessel being more or less, owing to the difference in the temperature which the supply-wires assume during the heating. These differences in the resistance of the heating-wire did not amount to more than 0.9 % in those cases where the resistance could be derived from the tension and current during the heating. They fall within the limits of accuracy which could be reached in these measurements [1]).

§ 2. *Specific heat of liquid hydrogen.* The correction to be applied for the evaporation of hydrogen during the calorimetric experiment is somewhat larger than in the case of nitrogen (Comm. N°. 149*a* § 5): the largest value was 4.5 % of the heat supplied.

The results are combined in table I and represented in fig. 2.

In this figure we have also included the results of EUCKEN's measurements [2]) (indicated by ΔΔ) concerning the specific heat of liquid hydrogen between 17.3° and 21.2° K. Our results, which, however, reach down to lower temperatures, agree at these higher temperatures with those of EUCKEN within the limits of accuracy of the measurements.

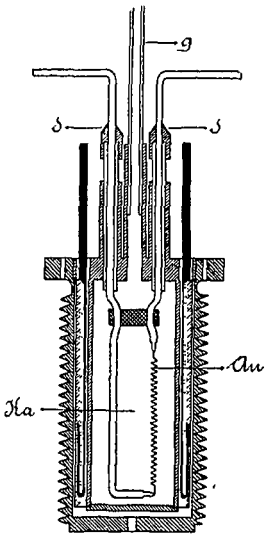

Fig. 1.

It is represented in Fig. 1. *Au* is the spirally wound wire of the purest gold to be obtained; diameter 0.05 mm., resistance at room-temperature 1,2 Ω. The spiral is suspended between two insulated supply-wires of gold (1 m.m.) which protrude through glass tubes through the lid of the copper chamber *Ka*. The glass tube *g* serves for filling the chamber with gas ($H_2$ or He). A constantin wire with platinum supply wires was wound round the chamber in exactly the same manner as described in Comm. N°. 143 § 2, to which we here refer. Special tests showed that at the temperature of liquid hydrogen the resistance of a spiral of the same gold wire, suspended in a space filled with gaseous hydrogen, could be measured with a current of 35 milli-ampères, without the Joule-heat raising the temperature of the wire by more than 0.01 of a degree above that of the bath.

The resistance of the gold wire which after winding is heated to 300° C. does not attain constant values, until it has been cooled in liquid air several (say 5 or more) times and brought back to room-temperature.

[1]) Our thanks are again due to Mr. J. M. BURGERS for his assistance in the temperature-measurements.

[2]) A. EUCKEN, Verh. d. physik. Ges. 1916, p. 4.

TABLE I.

Specific heat of liquid hydrogen.

| Number | Quantity of hydrogen in gr. | Mean temp. | Rise of temp. | Heat-capacity of hydrogen + flask and block $K_{III}$ in Joules p. degree K. | Heat-capacity of flask + block in Joules p. degree K. | Specific heat of hydrogen in $cal._{15}$ per degree K. | Atomic heat in $cal._{15}$ per degree K. |
|---|---|---|---|---|---|---|---|
| Febr. 12 '16 | 2.89 | 16.03$^5$ | 2.64 | 24 06 | 1 48 | 1.87 | 1.88 |
| April 12 VI | 3.17 | 15.81 | 0.54 | 23.98 | 1.43 | 1 70 | 1.71 |
| VII | „ | 16.80 | 0.50 | 26.05 | 1.63 | 1.84 | 1.85$^5$ |
| May 11 II | 3 52 | 14.71 | 0.54 | 25.84 | 1.22 | 1.67 | 1.68 |
| III | „ | 15.38 | 0.51 | 27 58 | 1.34$^5$ | 1.78 | 1.79 |
| Nov. 3 [1]) I | 3.50 | 14.82$^5$ | 1.24 | 26.73 | 1.24 | 1.74 | 1.75 |
| II | „ | 16.30 | 1.12 | 28.69 | 1.53 | 1.85 | 1.87 |
| III | „ | 17.63 | 1.04$^5$ | 30.97 | 1.81 | 1 99 | 2.00 |
| IV | „ | 18.67 | 0.61 | 32.54 | 2.06 | 2 08 | 2.09 |
| V | „ | 19.41 | 0.58 | 34.24 | 2.26 | 2.18 | 2 20 |
| VI | „ | 20.11 | 0 56 | 35.30 | 2.45 | 2.24 | 2.26 |
| Sept. 11 '17 [1]) II | 3.51 | 15.24$^5$ | 1.01 | 28.28 | 1.33 | 1.84 | 1.82 |
| III | „ | 16.37 | 0.95 | 29.49 | 1 54 | 1.90 | 1.89 |
| IV | „ | 17 37$^5$ | 0.92 | 30.98 | 1.75 | 1.99 | 1.98 |
| V | „ | 19.07 | 0.58 | 34.07 | 2.17 | 2.17 | 2.16 |

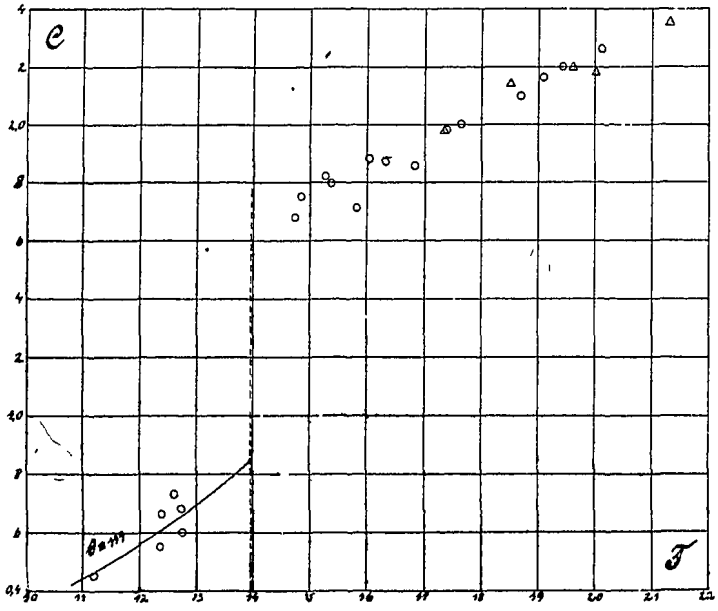


Fig. 2.

[1]) These measurements were carried out after this communication had been presented to the R. Academy and are here included.

§ 3. *Preliminary results of measurements on the atomic heat of solid hydrogen.* In connection with our measurements on the specific heat of liquid hydrogen we also carried out some calorimetric experiments on solid hydrogen at temperatures which could be reached by reducing the pressure as far as possible. As we have not had an opportunity to calibrate the thermometer-wire at these temperatures we can only give some preliminary results. They are based on the assumption that the linear dependence on the temperature which holds for the constantin wire between 14.16° and 20.48° K. with great accuracy (Comm. N°. 143, Oct. 14, Table I) remains valid for this wire down to 10.5° K. (or at least: down to 11.8° K., if the measurement of Oct. 23 I which is less certain on account of an insufficient vacuum in the calorimeter-vessel is excluded).

These results are also shown in fig. 2.

TABLE II.

Atomic heat of solid hydrogen. Preliminary results.

| Number | Quantity of hydrogen in gr. | Mean temp. | Rise of temp. | Heat-capacity of hydrogen + flask and block $K_{III}$ in Joules p. degree K. | Heat-capacity of flask and block $K_{III}$ in Joules per degree K. | Atomic heat of hydrogen in $cal_{15}$ per degree K. |
|---|---|---|---|---|---|---|
| April 12 '16 I | 3.17 | 12.61$^5$ | 1.31 | 10.51 | 0.87 | 0.73 |
| II | „ | 12.72$^5$ | 1.39 | 9.84 | 0.89 | 0.68 |
| May 11 I | 3.52 | 12.34 | 1.11$^5$ | 8.89 | 0.83 | 0.55 |
| Oct. 23 I | 3.19 | [11.20$^5$ | 1.47 | 6.69 | 0.68 | 0.45] |
| II | „ | 12.73$^5$ | 1.07 | 8.91 | 0.89 | 0.60 |
| Sept. 11 '17 [1]) VI | 3.51 | 12.36$^5$ | 0.61 | 10.41 | 0.83 | 0.66 |

In cooling the solid hydrogen for the object of these measurements, as also in a few special experiments made for this purpose, cooling curves (comp. Comm. N°. 149*a* fig. 5) were recorded. In several of them small irregularities occurred; as these did not show themselves at the same temperatures in all the curves, and even in two of them taken under the same circumstances were completely absent, we ascribe these bends to disturbances (such as changes of the galvano-

[1]) Comp. p. 1002 note.

meter-zero, change of temperature by radiation [1]), in the measurements of Febr.—May 1916 possibly owing to the formation of gaseous spaces in the bath of solid hydrogen by the evaporation) and we conclude from the whole of eight cooling-curves, that our experiments do not give an indication of the existence of a point of transformation for solid hydrogen between the triple point solid-liquid-vapour and 10°.6 K. [2])

Taking as a mean for the specific heat of solid hydrogen at $T' = 12.55°$ K. the value 0.64, we find (neglecting the difference $C_v - C_{sat}$) in DEBIJE's formula for hydrogen $\theta = 111$ (comp. the curve in fig. 2). To an even higher degree than in the case of nitrogen this value is smaller than the one which would follow from LINDEMANN's formula (Comm. N°. 137*a* § 5), viz. $\theta = 212$. As for nitrogen (Comm. N°. 149*a* § 4) we conclude that presumably hydrogen in the solid condition is more-atomic in the sense given there.

§ 4. *Heat of fusion of hydrogen.* We have made two experiments (May 11 1916 and Sept. 11 1917) for the determination of the heat of fusion, by measuring the heat which had to be supplied to heat the flask with hydrogen from 0.2° and 0.7° respectively below to 0.9° and 1,6° respectively above the triple-point-temperature. These experiments gave for the heat of fusion per gramme of hydrogen: 13.3 and 16.4 $cal._{15}$ respectively, with a mean value of 15 $cal._{15}$.

[1]) It was also partly to obviate the radiation referred to here, which is due to the walls at a higher temperature, that the calorimeter-vessel was afterwards surrounded by a copper cylinder (comp. § 1).

[2]) On the linearly extrapolated temperature-scale of *Const.*3 (comp. the beginning of this §).