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Physics. — "On the measurement of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume, down to the freezing-point of hydrogen compared with each other, and with the platinum-resistance thermometer. By Prof. H. KAMERLINGH ONNES and G. HOLST. Communication Nº. 141a from the Physical Laboratory at Leiden.

## (Communicated in the meeting of May 30, 1914).

\$ 1. *Introduction.* The measurements which this paper deals with bring the investigations undertaken in Leiden for the purpose of establishing the scale of the absolute temperatures as far down as the freezing point of hydrogen, to a conclusion, in so far that a direct comparison has now been made between the helium and hydrogen scales, by measurements with a differential thermometer, which had the object to test the corrections to the absolute scale of temperatures below 0° C., obtained separately for the helium scale (in XIX of this series) and the hydrogen scale (partially given in **XVIII** of this series  $^{1}$ ). For the place which the mutual control of these corrections occupies in the more general investigation of the measurement of low temperatures which is being carried out in Leiden, we refer to § 6 Suppl. N<sup> $\circ$ </sup>. 34*a*. The test could be extended as far as the freezing point of hydrogen, after the compressibility of hydrogen vapour had been determined by KAMERLINGH ONNES and DE HAAS, Comm. Nº. 127c. (June 1912)<sup>2</sup>). Our comparison of the helium scale with the hydrogen scale 3) by means of the differential thermometer to which was added a new calibration of the Leiden standard platinum thermometer  $Pt_{I}$  (formerly  $Pt_{I}$ ) shows that a very satisfactory agreement has been attained in the temperature determinations.

<sup>1</sup>) Compare also H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Comm. N<sup>0</sup>. 101a. (Nov. 1907) § 1 under 4b.

<sup>2</sup>) In this Comm. a difference was discussed which existed between the temperature determination with a hydrogen thermometer according to the resistance thermometer Ptt', which was calibrated by means of it and the temperature determination by extrapolation of the isotherms. According to calculations by Dr. KEESOM, suggested by SACKUR's interesting investigation, this deviation might be connected with the theory of quanta (Comp. Suppl. N<sup>0</sup>. 30 and N<sup>0</sup>.  $34a \le 11$ ).

<sup>3</sup>) The comparison of the hydrogen and helium thermometers by TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1903), p. 105, has been discussed in Comm. N<sup>0</sup>. 102. In general their results are in good agreement with our measurements.

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§ 2. Apparatus. Two identical thermometers of Jena glass 16<sup>th</sup>, such as had been formerly used by H. KAMERLINGH ONNES and C. BRAAK, were connected to one manometer. The arrangement was otherwise exactly the same as that used before. The standardmeter was divided into 1/s m.m. and allowed a direct estimation of  $1/s_0$  m.m. This gave a considerable saving of time, as it made the use of the measuring eye-piece of the cathetometer unnecessary. The amount of gas in the capillary was measured by an auxiliary capillary ot much larger section, as described by CHAPPUIS.

Besides the two thermometer bulbs, the cryostat contained the platinum resistance thermometer  $Pt_I$  and a large pump, which provided for a good circulation of the liquid.

The hydrogen and the helium were purified by distillation, and were both free from other gases.

§ 3. Calculations. The temperature for each of the thermometers forming the differential thermometer was calculated from the formula given in Comm. N°. 95e, but with a few alterations. The expansion of the glass f(t) of the bulb was not calculated from the quadratic formula given there, but taken from a graphic representation in which the curve was drawn through the points experimentally determined and extrapolated by means of the expansion for a different kind of glass as determined by CH. LINDEMANN. The influence of the different temperature function for the expansion of the glass is about  $\frac{1}{100}$  at hydrogen temperatures, at all other temperatures it is negligible. Moreover the volume was divided into three parts. a. The bulb at the temperature t of the bath. b. The capillary in which the mean density of the gas was determined, by means of the auxiliary capillary : the mean density is proportional to  $\frac{h_0}{t}$ ,  $h^0$ 

being the pressure in the auxiliary capillary at  $0^{\circ}$ , '*h* the measured pressure. *c*. The steel capillary and the volume about the point, the temperature of which is the same as that of the room.

If we divide all the members of the above mentioned equation by the volume of the bulb it becomes

$$\frac{H_{t}}{1+\alpha t} \left[ 1 + f(t) + \frac{\beta}{V_{o}} + \frac{V_{cap}}{V_{o}} (1+\alpha t) \frac{h_{o}}{h} + \frac{V_{dead \ col}}{V_{o}} (1+\alpha t) \frac{273}{1+\alpha t_{k}} \right] = H_{o} \left[ 1 + \frac{\beta}{V_{o}} + \frac{V_{cap}}{V_{o}} \frac{h_{o}}{h} + \frac{V_{dead \ vol}}{V_{o}} \frac{273}{1+\alpha t_{k}} \right].$$

The provisional temperature, which is needed for the calculation of the various corrections, was calculated from the resistance of  $Pt_{t'}$ . Even  $\frac{H_t}{H_o}$  gives this temperature with sufficient accuracy. The zeropressure for the hydrogen thermometer was  $H_o = 1191$  m.m.<sup>1</sup>), for the helium thermometer  $H_o = 1124$  m.m. Circumstances unnecessary to be mentioned here, had prevented these pressures from being made more equal. A new set of determinations in which this will be attended to is planned. The pressure coefficient of hydrogen at the above mentioned pressure was taken at 0.0036628; for helium at 0.0036614, the value derived by KAMERLINGH ONNES<sup>2</sup>) from the isothermals at 0° C. and 100° C. If we calculate with the pressure coefficient 0.0036617 deduced from the isothermals of 20° C. and 100°C. we find, after the introduction of the necessary corrections, almost the same temperature on the absolute scale.

§ 4. Arrangement for the resistance measurement. In order to measure and to compare resistance thermometers two identical differential galvanometer circuits were fitted up according to KOHLRAUSCH's method. Both galvanometers can be read from one place, so that nearly simultaneous measurements can be made. This removes all irregularity in the temperature of the bath in the comparison of resistance thermometers. Two moving coil differential galvanometers from HARTMANN and BRAUN were used. With an additional resistance of  $\pm 1000 \ \Omega$  in each of the coils these are practically aperiodic in the measurement of resistances less than 130  $\Omega$ , as with all our other thermometers. The sensitivity is sufficient to measure  $\frac{1}{100000} \ \Omega$  with a current of  $\pm 5$  milliampères, while the condition of proportionality between deflection and current-strength is very well fulfilled.

Test-measurements have shown, that with this arrangement resistances of about 100  $\Omega$ , such as our thermometers have at ordinary temperature, can be compared to  $\frac{1}{10000}$  without any difficulty. Our

<sup>&</sup>lt;sup>1</sup>) At these pressures even at the melting point of hydrogen no attent on need be paid to the thermo-molecular pressure according to KNUDSEN (Comp. Suppl. N<sup>0</sup>. 34 § 7 and a Comm. by H. KAMERLINGH ONNES and S. WEBER which is shortly to be expected, on the determination of the temperatures which can be obtained with liquid helium).

<sup>&</sup>lt;sup>2</sup>) H. KAMERLINGH ONNES. Comm. No. 102b. The value is here increased by 0.0000001, in consideration of the value 273.09 since assumed for  $T_{0^0}$  C. Comp. H. KAMERLINGH ONNES und W. H. KEESOM. Die Zustandsgleichung. Math.Enz. V 10, Suppl. No. 23, Einheiten c, and § 82b.

experience with moving coil differential galvanometers, for this purpose at any rate is very favourable <sup>1</sup>).

In the manner described we attained a much greater rapidity of measurement than was possible by the method described in the previous papers of this series, and this in its turn increases the accuracy.

We must also refer to our experience with thermometers in which the wire was sealed to the glass (Comm. N<sup>o</sup>. 95 $b \le 1$ ). For temperatures above that of liquid air they are not unsuitable, although even here they are less constant than those with a free thread. After immersion in liquid hydrogen their resistance was found to have increased by about one tenth of an Ohm. Each further immersion in hydrogen carried with it a permanent change of resistance, so that we replaced these thermometers by other ones with free threads wound on porcelain tubes with a double screw thread baked in. After a thermal treatment, consisting in several immersions in liquid hydrogen followed by moderate heating, these became satisfactorily constant.

§ 5. Results. In the following table the results of our researches are found. The two first columns contain the hydrogen and helium temperatures calculated from the formula given above. Column 3 and 4 contain the corrected temperatures on the absolute scale deduced from the hydrogen and from the helium thermometer, column 5 contains the resistance of the platinum thermometer  $Pt_{I'}$ .

The agreement is on the whole very satisfactory.

We have already mentioned that with thermometers of the kind described an accuracy of about  $1/_{50}^{\circ}$  might be expected. Our measurements show this to be the case; only in a few points larger deviations occur. These can readily be explained by a small defect which will be avoided when we repeat the experiments, namely that the cryostat which had to be used was not quite symmetrically built. When both auxiliary capillaries worked properly this was not of much consequence. But (except fortunately in the determinations most important for us viz. at the hydrogen-temperatures) the helium capillary got out of order, so that the distribution of the temperature of the stem of the helium thermometer had to be deduced from the observations with the hydrogen capillary. This circumstance has the greatest influence at temperatures at which the methyl chloride and the oxygen evaporated under reduced pressure, and it is exactly there that the greatest deviations occur.

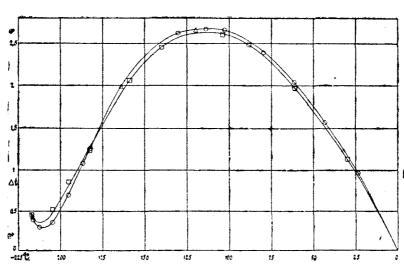
1) Compare JAEGER, Zeitschr. f. Instrumentenkunde 1904.

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	TABLE I.							
•	<i>t</i> <sub>H2</sub>	<sup>t</sup> He	$ heta_{H_2}$	$ heta_{He}$	W <sub>Pť</sub> I			
	0				135.450			
. 1	- 23.96	- 23.94	- 23.96	- 23.94	122.613			
2	43.09	43.07	43.09	43.07	112.278			
3	61.50	61.49	61.50	61.49	102.280			
4	79.57	79.51	79.57	79.51	92.422			
5	102.72	102.69	102.70	102.69	79.674			
6	113.58	113.55	113.56	113.55	73.629			
7	130.46	130.41	130.43	130.41	64.189			
8	182.88	182.81	182.82	182.79	34.180			
9	186.79	186.70	186.73	186.68	31.904			
10	195.24	195.15	195.18	195.13	26.988			
11	204.79	204.69	204.71	204.67	21.491			
12	212.61	212.52	212.52	212.50	17.097			
13	216.25	216.15	216.16	216.13	15.119			
14	252.80	252.68	252.66	· 252.64	1.924			
15	<b>256.2</b> 3	256.10	256.08	256.06 ·	1.601			
16	258.56	258.41	258.39	258.37	1.453			
17	252.80	4 A.	252.66		1.925			
18	253.78		253.64		1.819			
19	255.20		255.05		1.685			
20	257.22		257.05		1.531			

The readings of  $Pt_{I}$  allow a comparison with the measurements of 1906—1907.

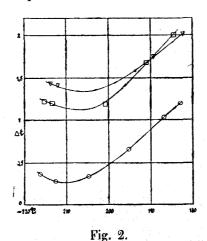
In fig. 1 the deviations from the linear formula  $t = -243 + 243 \frac{\nu}{W_0}$ are represented for all three calibrations, at temperatures above  $-217^{\circ}$  C. The circles refer to the calibration of 1913, the triangles to 1907 and the squares to 1906. For the calculation of temperatures in this field the above formula with the deviation curve belonging to it has been recently used in the Leiden researches.





The differences between the calibrations of 1913 and 1907 are less than  $\frac{1}{50}$ <sup>th</sup> of a degree throughout. The fact that the differences with the first calibration (1906) are more considerable must undoubtedly be attributed to the mechanical treatment of the wire: after the first calibration the wire broke, and had to be re-wound. It must be ascribed to chance, that the deviations are so small just at the points of the second calibration.

§ 6. The field of utility of the platinum resistance thermometer at low temperatures. Resistance thermometers for other fields of temperatures. The curve in fig. 1 shows at once the peculiar behaviour of platinum below  $-200^{\circ}$ . At this temperature a change of direction



in the line which gives the resistance as a function of the temperature is sharply marked. In fig. 2 the deviations from the formula given above in the oxygen field are once more represented (circles) and also those for the thermometers  $Pt_i$  (squares) and  $Pt_g$  (triangles), which were also directly compared with the hydrogen-thermometer by Dr. C. DORSMAN and us. It is clear from the curves that we have to deal with a specific peculiarity of platinum, which makes it very unsuitable to be used

as a thermometer in this field, as accurate interpolations are impossible. For this reason in the field of temperatures below  $-200^{\circ}$ C.

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a gold thermometer is preferable to a platinum one, as has already been pointed out by KAMERLINGH ONNES and CLAY<sup>1</sup>).

At hydrogen temperatures both platinum and gold are no longer approximately linear. Here and at helium temperatures manganine and constantin proved to be nearly linear and fit for resistance thermometers. Concerning these we refer to a future comm. dealing with resistance measurements in particular for the determination of the specific heat of mercury at helium temperatures.

§ 7. Comparison of our thermometer Pt1' with other platinum resistance thermometers. Comparing our measurements with those of F. HENNING<sup>2</sup>) formulae of the form:

$$\Delta R = M(R-1) + N(R-1)^2$$
 and  $\alpha' = \frac{\alpha^2 N}{c}$   $M = \frac{\alpha N}{c}(1-100c) - 1$ .

were used. This was done because there were objections to a direct determination of the temperature coefficient by measuring the resistance of  $Pt'_I$  at 0° C. and 100° C. which since the first calibration had never been brought to a temperature above the ordinary. We found 117

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	$R \equiv \frac{w}{m}$	$R = \frac{W}{W}$							
	$W_{0}$	$R \equiv \overline{W_{0}}$							
t	(K.O. and H.)	(Henning)	$10^{\circ} \Delta R$	$R_{1}$					
23.96	0.90523	0.90449	74	0.09551					
43.09	0.82893	0.82775	118	0.17225					
61.50	0.75511	0.75340	171	0.24660					
79.57	0.68233	0.67989	<b>237</b>	0.32011					
102.72	0.58822	0.58492	330	0.41508					
113.58	0.54359	0.54007	352	0.45993					
130.46	0.47389	0.46986	403	0.53014					
182.88	0.25234	0.24686	<b>548</b>	0.75314					
186.79	0.23554	0.22998	556	0.77002					
These numbers give: $M = -0.0078758$									
N = -0.0007605.									

And further

$$100a' = -0.38821$$

 $c = -0.30.10^{-5}$ 

From the results it appears that our platinum thermometer, as regards its constants, lies between the platinum thermometers Nº. 1 and N<sup>o</sup>. 7 used by HENNING in his investigation. This was to be expected, as these thermometers, like ours, were obtained from HERAEUS, Nº. 1 and Ptr' being of earlier date. The difference with the values calculated by HENNING is caused by the fact that his calculation was based on our calibration of 1906, which differs from our present one and that of 1907 (Comp. § 5).

1) Comm. Nº. 95. Used also by CROMMELIN, Comm. Nº. 140a.

2) Ann. der Phys. 4te Folge Bd. 40, 1913.