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**Physics.** — “*On the measurement of very low temperatures*”. XXVI.

*The vapour-pressures of oxygen and nitrogen according to the pressure-measurements by v. SIEMENS and the temperature-determinations by KAMERLINGH ONNES c. s. By Dr. G. HOLST.*

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(Communicated by Prof. H. KAMERLINGH ONNES).

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§ 1. *Introduction.* The main object of this communication is a correction of the calculation of the results contained in a paper by H. VON SIEMENS, *Annalen der Physik* Vol. 42, p. 871, 1913. SIEMENS determined the vapour-pressure as a function of the temperature for a number of substances using a platinum-resistance-thermometer. This thermometer had been reduced to the Leiden-standard-platinum-thermometer  $Pt_1$  by means of NERNST's linear reduction-formula. For a handy calculation of the temperatures SIEMENS used an interpolation-table in which the resistance is given divided by the resistance at  $0^\circ\text{C}$ . below  $80^\circ\text{K}$ . for every two degrees and for temperatures between  $80^\circ\text{K}$ . and  $290^\circ\text{K}$ . for every five degrees. For this purpose he used the data of the Leiden-calibration of 1905—1906. It has appeared, however, afterwards that this calibration does not agree so well with subsequent ones as these among themselves and that, particularly in the oxygen-region, considerable deviations occur which must therefore also affect the results obtained by SIEMENS. We will therefore begin by a detailed examination of these deviations.

§ 2. *The calibration of  $Pt_1$ .*

The first comparison of this resistance-thermometer with the hydrogen-thermometer was carried out in 1905—1906 by KAMERLINGH ONNES, BRAAK and CLAY. The results are contained in the table on p. 44 of Comm. 95c. Subsequently  $Pt_1$  broke and was then once more wound. The repaired thermometer was called  $Pt'_1$ . It was again compared with the hydrogen-thermometer in 1907. On page 5 of Comm. 101a its resistance at nine different temperatures is given. Small differences showed themselves at the time up to 0,04 of a degree. In the end of 1907 and the beginning of 1908 another calibration was performed at six different points: the results were published in Comm. 107a page 6.

In 1913 a new series of measurements was made by KAMERLINGH ONNES and HOLST, the results being contained in Table 1 Comm. 141a page 7.<sup>1)</sup>

<sup>1)</sup> An interpolation-formula representing these observations between  $15^\circ\text{K}$ . and  $230^\circ\text{K}$ . was given by ZERNIKE. (*These Proceedings Kon. Ak v. Wet.* XXIII, p. 742, 1914).

TABLE 1.					
Resistance of the platinum-thermometer $Pt_1$ by KAMERLINGH ONNES c.s.					
$T_{\text{abs. scala}}$	$\frac{W}{W_0}$	diff.	$T_{\text{abs. scala}}$	$\frac{W}{W_0}$	diff.
56° K.	0.10815	374	74° K.	0.18252	427
57	11189	394	75	18679	427
58	11583	401	76	19106	428
59	11984	406	77	19534	428
60	12390	409	78	19962	428
61	12799	411	79	20390	429
62	13210	412	80	20819	429
63	13622	414	81	21248	430
64	14036	416	82	21678	431
65	14452	417	83	22109	431
66	14869	418	84	22540	430
67	15287	420	85	22970	431
68	15707	421	86	23401	430
69	16128	423	87	23831	431
70	16551	424	88	24262	430
71	16975	425	89	24692	431
72	17400	426	90	25123	430
73	17826	426	91	25553	

On the basis of the results of the last three calibrations I have now computed a new interpolation-table, in which the resistance-ratio is given from 56° K. to 91° K. for every degree and from 90° K. to 270° K. for every five degrees. This table ought to replace the one given by SIEMENS and at the same time for temperatures below 80° K. supplement the full table computed by HENNING<sup>1)</sup>. This addition may be useful, although it must not be forgotten, that exactly in the range below 80° K. the platinum-thermometer gives rise to special difficulties<sup>2)</sup>.

<sup>1)</sup> F. HENNING Ann. d Phys 40, p. 635, 1913.

<sup>2)</sup> Comp. Comm. Leiden 141a § 6.

TABLE 1 (continued).					
Resistance of the platinum-thermometer $Pt_1$ by KAMERLINGH ONNES c.s.					
$T$ abs. scale	$\frac{W}{W_0}$	diff.	$T$ abs. scale	$\frac{W}{W_0}$	diff.
90° K.	0.25123		185° K.	0.64776	
		429.8			405.6
95	27272	428.8	190	66804	404.4
100	29416	427.2	195	68826	403.4
105	31552	425.6	200	70843	402.8
110	33680	423.8	205	72857	402.2
115	35799	422.2	210	74868	401.8
120	37910	420.8	215	76877	401.4
125	40014	419.4	220	78884	401.0
130	42111	418.0	225	80889	400.6
135	44201	416.6	230	82892	400.0
140	46284	415.2	235	84892	399.2
145	48360	413.8	240	86888	398.4
150	50429	412.6	245	88880	397.8
155	52492	411.6	250	90869	397.0
160	54550	411.0	255	92854	396.2
165	56605	410.4	260	94835	395.4
170	58656	409.2	265	96812	394.4
175	60702	408.0	270	98784	393.4
180	62742	406.8	273.09	1.—	

The temperatures given in Table 1 are those read on the hydrogen-thermometer and corrected to the absolute scale, for the latter purpose the corrections as determined by KAMERLINGH ONNES and BRAAK <sup>1)</sup> being used.

In order to be able to form an opinion of the accuracy of this table I have calculated for all four calibrations the temperature corresponding to  $\frac{W}{W_0}$  according to the table, and the deviations from the temperatures, as observed.

<sup>1)</sup> Comm. Leiden 101b.

TABLE II.			
Comparison of different calibrations of $Pt_1$ .			
$\frac{W}{W_0}$	$T_{\text{table}}$	$T_{\text{obs. and corr. to abs. scale.}}$	$T_{\text{observ. — calc.}}$
Calibration 1905 1906. Comm. 95c p. 44.			
1.	273.09° K.	273.09° K.	0.
0.88180	243.24	243.29	+ 0.05
76° 15	214.35	214.34	— 0.01
64749	181.93	184.96	+ 0.03
58345	169.24	169.28	+ 0.04
43450	133.20	133.25	+ 0.05
35486	114.26	114.30	+ 0.04
25280	90.36 <sup>5</sup>	90.36	— 0.00 <sup>5</sup>
20013	78.12	77.97	— 0.15
15969	68.61	68.47	— 0.14
12539	60.36	60.34	— 0.02
10709	55.72	55.76	+ 0.04
Calibration 1907. Comm. 101a p. 105.			
0.58426	169.44	169.44	0.00
51825	152.38 <sup>5</sup>	153.38	— 0.00 <sup>5</sup>
33265	109.02 <sup>5</sup>	109.02	— 0.00 <sup>5</sup>
25467	90.80	90.80	0.00
11028	56.57	56.56	— 0.01

As will be seen the first calibration shows pretty considerable deviations, whereas the others are in very good agreement with each other. Only at one point a deviation of 0.03 of a degree occurs, which is not more than might be expected considering that the accuracy of the hydrogen-thermometer is not much greater than 0.02 of a degree.

TABLE II (continued).			
Comparison of different calibrations of $Pt_1$ .			
$\frac{W}{W_0}$	$T_{\text{table}}$	$T_{\text{obs. and corr.}}$ to abs. scale	$T_{\text{obs.}-\text{calc.}}$
Calibration 1907—1908. Comm. 107a p. 6.			
0.25369	90.57	90.55	— 0.02
23647	86.57	86.55	— 0.02
22395	83.66	83.65	— 0.01
10945	56.35	56.33	— 0.02
25294	90.40	90.41	+ 0.01
25044	89.82	89.85	+ 0.03
Calibration 1913. Comm. 141a p. 7.			
0.90523	249.13° K.	249.13° K.	0.00
82893	230.00	230.00	0.00
75511	211.60	211.60	0.00
68233	193.53	193.53	0.00
58820	170.40	170.39	— 0.01
54359	159.53 <sup>s</sup>	159.53	— 0.00 <sup>s</sup>
47389	142.66	142.66	0.00
25234	90.26	90.27	+ 0.01
23554	86.36	86.36	0.00
19925	77.91	77.91	0.00
15866	68.38	68.38	0.00
12622	60.57	60.57	0.00
11162	56.93	56.93	0.00

§ 3. Comparison of  $Pt_1$ , with  $P_{32}$  of HENNING<sup>1)</sup>.

We will now compare the scale as laid down in our table with that determined by HENNING for his platinum-thermometer  $P_{32}$ ; for this purpose HENNING's values were first reduced to the absolute scale according to KAMERLINGH ONNES, and BRAAK's corrections<sup>2)</sup>.

<sup>1)</sup> F. HENNING. Ann. d. Phys. (40), 635, 1913.

<sup>2)</sup> Comm. Leiden 101b.

TABLE III.			
Comparison of the platinum-thermometer of KAMERLINGH ONNES c.s. ( $Pt_1$ ) with that of HENNING $Pt_{32}$ .			
$T$	$\left(\frac{W}{W_0}\right)_{Pt_1}$	$\left(\frac{W}{W_0}\right)_{P_{32}}$	$\Delta$
80° K.	0.20819	0.20241	0.00578
100	29416	28881	535
120	37910	37432	478
140	46284	45874	410
160	54550	54200	350
180	62742	62448	294
200	70843	70624	219
220	78884	78737	147
240	86888	86787	101
260	94835	94786	049
273.09	1. —	1. —	0. —

We shall first try to reduce the two scales to each other by means of NEURST's linear formula. For this purpose we can utilize the fact, that on both thermometers the boiling point of oxygen was measured; at this point  $Pt_1$  gave  $\frac{W}{W_0} = 0.25176$ , and  $P_{32}$   $\frac{W}{W_0} = 0.24631$ <sup>1)</sup>, so that in the formula

$$\Delta \left( \frac{W}{W_0} \right) = \alpha \left( 1 - \left( \frac{W}{W_0} \right)_{Pt_1} \right)$$

$$\alpha = 0.007284.$$

If we do not want to go beyond an accuracy of  $\frac{1}{20}$  of a degree, we may use this linear relation<sup>2)</sup>. A much closer correspondence is obtained, however, if with HENNING<sup>3)</sup> we use a quadratic relation.

<sup>1)</sup> F. HENNING. Ann. d. Phys. (43), 282, 1914.

<sup>2)</sup> H. SCHIMANK. (Ann. d. Phys. (45), 706, 1914) states, that, for  $\alpha = 0.03$ , a difference of 0.1–0.2 of a degree is to be expected, which agrees with the difference found here of  $\frac{1}{20}$  of a degree for  $\alpha = 0.0073$ .

<sup>3)</sup> F. HENNING. Ann. d. Phys. (40), 635, 1913.

Even then, however, real deviations remain in the range 200° K. - 240° K. showing that the Leiden-temperature-scale lies here somewhat above that of the Phys. Techn. Reichsanstalt.

TABLE IV.					
Comparison of the linear and the quadratic deviation-formulae.					
$T$	$\Delta W_{\text{obs.}}$	$\Delta W_{\text{calc.}}$ NERNST	$\Delta T_{Pt'_1-Pt_{32}}$	$\Delta W_{\text{calc.}}$ quadr. form.	$\Delta T_{Pt'_1-Pt_{32}}$
80° K.	0.00578	0.00576	- 0.005	0.00578	0.00
100	535	514	- 0.05	525	- 0.02
120	478	452	- 0.06	470	- 0.02
140	410	391	- 0.045	408	- 0.00
160	350	331	- 0.045	355	+ 0.01
180	294	271	- 0.06	296	0.00
200	219	212	- 0.02	235	+ 0.04
220	147	154	+ 0.02	173	+ 0.06
240	101	096	- 0.01	108	+ 0.02
260	049	038	- 0.03	044	- 0.01
273.09	0	0	0	0	0

A good correspondence at the lower temperatures is obtained with the following formula

$$\Delta \left( \frac{W}{W_0} \right) = 0.00850 \left( 1 - \frac{W}{W_0} \right) - 0.001515 \left( 1 - \frac{W}{W_0} \right)^2.$$

The greatest deviation amounts to 0.06 of a degree at 220° K. It would seem to me, that this formula cannot be far wrong, and for the following reasons. Looking at fig. 2 on page 653 in HENNING'S paper, we see that the curve  $T-T_C$  as a function of the temperature, in the temperature region under consideration, allows a small shift upwards, without the agreement with the observations becoming much impaired, which shows, that the deviation from CALLENDAR'S formula begins even at a somewhat higher temperature.

In the range in question we can further utilize the freezing point of mercury. HENNING<sup>1)</sup> has made a very accurate measurement of this

<sup>1)</sup> F. HENNING. Ann. d. Phys. (43), 282, 1914.



point, from which may be inferred that  $\frac{W}{W_0} = 0.84465$  at this point. According to the quadratic formula we should then have for  $P_{t_1}' \frac{W}{W_0} = 0.84593$  corresponding to  $-38^\circ.84$  C., whereas the temperature-scale of the P. T. R. gives  $-38^\circ.89$ . Borrowing from HENNING's paper the results of other observers:

STEWART	— 38.85
CHAPPUIS	— 38.80 ± 0.02
CHREE	— 38.86

we see that the freezing point as determined by HENNING, when reduced to the Leiden scale, coincides exactly with the mean of the other observers. Although this must, of course, not form the basis of a final judgment on the difference of the two temperature-scales, still we may see in it an indication of the cause of the deviation, viz. too great a value having been attributed to CALLENDAR's formula at temperatures below  $-20^\circ$  C.

Each fresh direct determination of the freezing point of mercury may, moreover, lead to a decision in favour of one or the other of the two temperature-scales.

Apart from the deviation just discussed, the agreement is a very good one, no greater deviations occurring than of 0.02 of a degree. It remains a matter for regret, however, that for  $P_{t_1}'$  the constants of CALLENDAR's formula were not determined, before proceeding to use the thermometer at low temperatures, which would have made a more direct comparison possible. With a view to the great importance of  $P_{t_1}'$  for low temperature-thermometry it was not deemed advisable to carry out the determination in question now. <sup>1)</sup>

#### § 4. *The vapour-pressure of oxygen.*

KAMERLINGH ONNES and BRAAK have determined the vapour-pressure of oxygen at four different temperatures. As the resistance of  $P_{t_1}'$  was measured at the same time, these vapour-pressures may be reduced to the temperature-scale as laid down in the above table.

We find, that the temperature corresponding to a given vapour-pressure may be represented by the following formula which is of the form as proposed by AUGUST—RANKINE—VAN DER WAALS.

$$T = \frac{369.83}{6.98460 - \log p}$$

HENNING also gives the vapour-pressure at a few temperatures in

<sup>1)</sup> Comp Comm. Leiden N<sup>o</sup>. 141a

the neighbourhood of the boiling point. Calculating according to the above formula the temperatures corresponding to these vapour-pressures we do not find greater deviations than of 0.02 of a degree, so that the temperature belonging to a given vapour-pressure is pretty sure to be accurate to 0.02 of a degree.

TABLE V.				
Vapour-pressures of oxygen according to KAMERLINGH ONNES and BRAAK.				
$\frac{W}{W_0}$	$p$ mm.	$T_{\text{table}}$	$T_{\text{K.O. and B.}}$	$T_{\text{formula}}$
0.25424	807.18	90 70° K.	90.68° K.	90.70° K.
25176	760.16	90.12	90.10	90.12
23647	516.19	86.57	86.55	86.57
22395	366.24	83.66	83.65	83.66

TABLE VI.			
Vapour-pressures of oxygen according to HENNING.			
$T_{\text{reduced to abs. scale}}$	$p$	$T_{\text{formula}}$	$\Delta T$
88.305° K.	626.7	88.315° K.	- 0.01
88.805	659.8	88.79	+ 0.015
90.115	758.0	90.095	+ 0.02
90.114	758.7	90.105	+ 0.01
90.171	764.0	90.17	0.00

By means of the formula given above the vapour-pressure measurements by SIEMENS may now be recalculated. SIEMENS gives the resistance of his thermometer at an oxygen-pressure of 766.8 mm., where according to the formula  $T = 90^{\circ},21$  K. According to the table at this point the resistance-ratio for  $Pt_1$  is 0.25211, whereas for SIEMENS' thermometer it is 0.25923, so that  $\alpha$  in NERNST's linear formula is equal to 0.00961; with this constant the thermometer may be reduced to  $Pt_1$  and the temperatures may be calculated.

It follows from the value of  $\alpha$ , in connection with what was found above in the comparison between  $Pt_1$  and  $P_{32}$ , that no greater

TABLE VII.				
Vapour-pressures of oxygen. Pressures by SIEMENS, temperature by KAMERLINGH ONNES c.s., as calculated by HOLST.				
$W$	$\frac{W}{W_0}$	$\left(\frac{W}{W_0}\right)_{P_{t_1}}$	$T_{\text{abs. scale}}$	$p_{\text{mm.}}$
32.597	0.25924	0.25212	90.21° K.	766.8
30.083	0.23924	23193	85.52	457.6
27.341	0.21743	20991	80.40	239.5
25.068	0.19936	19167	76.14	129.5
23.262	0.18500	17717	72.74	75.7
20.400	0.16224	15419	67.31	28.07
18.244	0.14509	13687	63.16	11.52
16.648	0.13240	12406	60.04	5.49
16.253	0.12926	12089	59.26	4.40
15.327	0.12189	11345	57.40	2.68

accuracy may be expected than to about 0.05 of a degree. The corrections for Stock's thermometer also undergo a change and become as given in Table VIII.

TABLE VIII.			
Corrections for Stock's thermometer according to Table VII			
$t_{\text{obs.}}$	$t_{\text{corr.}}$	$t_{\text{obs.}}$	$t_{\text{corr.}}$
- 183	- 183.96° C.	- 192	- 192.44° C.
- 184	- 184.90	- 193	- 193.41
- 185	- 185.83	- 194	- 194.44
- 186	- 186.79	- 195	- 195.42
- 187	- 187.76	- 196	- 196.39
- 188	- 188.68	- 197	- 197.33
- 189	- 189.62	- 198	- 198.34
- 190	- 190.54	- 199	- 199.37
- 191	- 191.50	- 200	- 200.40

§ 5. *The vapour-pressures of nitrogen.*

The deviations of the scale used by VON SIEMENS from the Leiden scale having been computed in the case of oxygen, SIEMENS' temperatures for nitrogen can be corrected directly. Table IX gives the results

TABLE IX.	
Vapour-pressures of nitrogen. Pressure by SIEMENS, temperature by K. ONNES C.S., as calculated by HOLST.	
<i>T</i> abs. scale	<i>p</i> m.m.
80.48° K.	1086.0
79.82	1009.4
75.86	631.3
72.85	428.6
70.97	329.4
67.89	206.9
66.93	117.6
63.25	93.5
63.25	93.5
62.87	86.1
62.02	71.9
60.83	55.3
60.01	45.8
58.76	34.1
57.73	26.4
57.00	21.8