

Citation:

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Physics. — “*The specific heat at low temperatures. II. Measurements on the specific heat of copper between 14 and 90° K.*” By W. H. KLEESOM and H. KAMERLINGH ONNES. Communication N°. 147*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 26, 1915).

§ 1. In Comm. N°. 143 (Oct. 1914, These Proceedings Dec. 1914) § 6 we published a series of measurements on the specific heat of copper between 15 and 22° K. We have since made some improvements in the experimental arrangement, particularly as regards the resistance measurement for the purpose of the determination of the temperature increase in the calorimetric experiment. The determination of the “sensitivity” of the THOMSON-bridge arrangement (cf. Comm. N°. 143 § 2) was made this time by shunting the standard resistance of 1 Ω (cf. Comm. N°. 143 Fig. 5) by a known resistance and reading the resulting galvanometer deflection. Irregularities as mentioned in Comm. N°. 143 § 4 note 1 did not occur now.

At a new calibration of the thermometer wire Au_{c3} it appeared not to have remained so constant, especially at liquid hydrogen temperatures, as at the time of the measurements of Comm. N°. 143 we concluded from determinations in liquid hydrogen on two different days (table I Comm. N°. 143), and also from the comparison of the result of a control measurement¹⁾ at the boiling point of oxygen on May 25 with the results of the measurements of May 18 1914. See table I.

Hence the resistance of the gold wire Au_{c3} ²⁾, which is enclosed in enamel between metal, appears to show small differences when brought to the same temperature at different times. This behaviour agrees with what has been experienced with wires sealed in glass: cf. KAMERLINGH ONNES and HOLST, Comm. N°. 141*a* § 4.

At liquid oxygen temperatures the differences are, however, so small, that for the calorimetric determination at these temperatures they are unimportant. At liquid hydrogen temperatures account has to be taken of these changes.

¹⁾ This control measurement, which was not mentioned in Comm. N°. 143, gave:

	T	$W_{Au_{c3}}$
May 25 '14	90.45	3.6616

²⁾ The preliminary treatment consisted in (cf. Comm. N°. 143 § 3): glowing before the winding, then 6 times cooling in liquid air and allowing it to return to room temperature, likewise 2 times in liquid hydrogen.

TABLE I. Resistance of Au_{c3} .				
No.	T	W	Standard-thermometer	$\frac{W}{\bar{W}_{\text{May '14}}}$
27 Febr. '15	II 14.10	0.6164	H_2 vapour pressure apparatus	1.0034
	III 16.97	0.6437		34
	I 20.41	0.6952		33
25 Febr. '15	II 56.94	2.0822	Pt_{γ}	[1.0033] ²⁾
	III 60.65	2.2582		
	IV 68.65	2.6385		
	V 77.93	3.0779		
	VI 86.41	3.4759		
	I 90.28	3.6550		
30 April '15	II 14.49	0.6188	Pt_{γ} ¹⁾	1.0023
	IV 16.97	0.6432		25
	III 18.49	0.6633		24
	I 20.49	0.6954 ⁵⁾		15
12 May '15	II 60.69	2.2580	Pt_{γ} with changed zero resistance, calculated from the resistance of Pt_{γ} at points III and IV.	[1.0027] ²⁾
	III 68.77	2.6429		1.0004
	IV 77.84	3.0718		0.9997
	I 89.89	3.6360		0.9999
	V 89.89	3.6368		0.9999

This was done for the measurements treated in this paper by determining for each series of measurements in liquid hydrogen a point of the scale of Au_{c3} with the aid of the temperature derived from the pressure of the liquid hydrogen bath³⁾.

¹⁾ Checked by comparison with the temperatures calculated from the pressure of the bath.

²⁾ It has appeared since that at this temperature the calibration of the auxiliary thermometers used in the measurement of May '14 was less accurate.

³⁾ In table I it appears from the measurements of April 30 '15 that even in a single series of measurements at hydrogen temperatures small changes in Au_{c3} may occur. With a view to this fact we intend in future measurements to determine each time at least two points of the scale of Au_{c3} , viz. one at the boiling point and one at the melting point of hydrogen.

§ 2. *Heat capacity of the core K_{III} .* With a view to the irregularities which had occurred in the measurements of 1914 (Comm. N^o. 143 § 4) this heat capacity was determined once more. In these measurements at a pressure of 75.6 cms. of the hydrogen bath, which corresponds to $T=20.31$, $W_{\Delta u_{c3}}$ was found equal to 0.6940 Ω , whereas according to the calibration of Febr. 27, '15 this resistance corresponds to $T=20.34$. The difference between these two values of T corresponds to a displacement of the curve, which represents the heat capacity of K_{III} as a function of the temperature to an amount of 0.3 % of the heat capacity at 15° K., and to an appreciably smaller amount at 20° K. As this is far within the limit of accuracy reached in the measurements the calibrations of 25/27 Febr. '15 could be used for the calculation of the temperatures.

TABLE II. Heat capacity of the core K_{III} .				
N ^o .	Mean temperature	Temperature increase	Heat capacity in joules/degree K.	
27 Jan. '15	II	14.81 ⁵	1.018	0.714
	III	15.07	1.174	0.732
	IV	15.87	1.227	0.822
	V	18.02	1.171	1.082
	VI	20.56	0.895	1.419
	I	20.86 ⁵	1.005	1.488
	VII	25.40	0.856	2.29
	VIII	30.33	0.939	3.32 ⁵
	IX	39.91	0.856	6.23
	X	49.91	0.736	9.43
28 Jan. '15	I	60.13	1.024	12.66
	II	61.04	0.993	12.73
	III	70.40	0.834	15.27
	IV	80.58	0.718	17.44
	V	81.10	0.701	17.95
	VI	89.01 ⁵	0.768	19.45
	VII	89.57 ⁵	0.758	19.49

The heat capacity appears to be a little smaller in the region of the liquid hydrogen temperatures in these measurements than at

those of 1914, viz. 0.023 joules/degree at 15° K., and 0.038 joules/degree at 20° K.¹⁾

This difference can be explained by the fact that for the measurements of 1915 on K_{III} for the wires which carry the heating current a little less platinum had been used. This circumstance was taken into account as far as possible.

§ 3. *Atomic heat of copper.*²⁾ For the measurements the same block of copper was used as for those of Comm. N°. 143 § 6: electrolytic copper of FELTEN and GUILLAUME, 596,0 grammes.

As a check on the purity of the copper after the measurements a strip was cut from the block; the strip was filed to a rectangular section, then rolled and annealed. The resistance was then measured at room temperature and in liquid hydrogen³⁾.

¹⁾ The measurements of 1914 being corrected for the change of A_{uc} .

²⁾ The atomic heat of copper has already been measured between 23 and 88° K. by W. NERNST, Ann. d. Phys. (4) 36 (1911), p. 395.

³⁾ We took advantage of this opportunity to test at the same time the purity of the lead which we had used for the measurements on this metal of Comm. N°. 143, and to investigate the influence of the treatment of the metal on the decrease of the resistance. The results are collected in the following table.

	$\frac{W_{20.36^\circ K}}{W_{11.8^\circ C}}$	$\frac{W_{17.0^\circ K}}{W_{11.8^\circ C}}$	$\frac{W_{14.93^\circ K}}{W_{11.8^\circ C}}$	$\frac{1}{W_{0^\circ C}} \cdot \frac{dW}{dT}$ at 10° C.
Copper filed	0.01287		0.01229	0.00426
" rolled	0.02359	0.02311	0.02295	420
" " and annealed	0.01042		0.00982	430
Lead cut	0.02827		0.01229	411
" rolled	0.02828		0.01222	410

These data lead to the following conclusions regarding the influence of the treatment of the metal on the change of the resistance with change of temperature:

For *copper* rolling diminishes the decrease of the resistance between room temperature and the boiling point of hydrogen in a large degree.

By subsequent annealing the influence of rolling the copper is not only annulled, but the decrease of the resistance between the temperatures mentioned above is now even greater than that of copper which has not been rolled and annealed; apparently annealing has also annulled the influence of previous mechanical treatment (filing), probably in consequence of the fact that the metal has united again to larger crystals.

The temperature-coefficient at hydrogen temperatures undergoes only a small change by the manipulations mentioned above.

The change of the resistance of *lead* suffers not only a small change by rolling.

$$\frac{W}{W_{11.8^{\circ}\text{C}}} = 0.0104 \text{ at } 20.4^{\circ}\text{K.} \\ = 0.0098 \text{ at } 14.9^{\circ}\text{K.}^1)$$

The temperature coefficient at 10°C. was also determined by measurements at 0 and 20°C. :

$$\frac{1}{W_{0^{\circ}\text{C}}} \cdot \frac{dW}{dT} = 0.00430 \text{ at } 10^{\circ}\text{C.}$$

These values point to a high degree of purity, which is certainly sufficient for the measurements on the atomic heat ²⁾.

In the measurements in hydrogen at a pressure of the bath of 75.2 cms, to which belongs $T = 20.30$, $Au_{0.3}$ was found equal to 0.6932Ω . According to the calibration of Febr. '15 this resistance corresponds to $T = 20.29$. The agreement between these values of

No.	Mean temperature	Temperature increase	Heat capac. of copperblock + core in joules/degree K.	Atomic heat in cal ₁₅ /degree K.		θ
				C_p	C_v	
16 Dec. '14	II	14.51	1.206	2.246	0.0396	330
	III	15.59 ⁵	0.955	2.791	506	326
	IV	17.17	1.047	3.691	687	325
	V	20.19 ⁵	1.065	5.959	0.1155	321
	I	20.74 ⁵	0.880	6.255	1217	324
	VI	25.37	0.918	11.42	234	319
	VII	29.73	0.667	18.01	377	317
	VIII	40.22	0.822	40.55	870	315
	IX	50.04	0.672	66.38	1.434	315
15 Jan. '15	I	59.75	0.537	94.42	2.06	310.5
	II	60.33	0.540	95.40	2.08	312
	III	69.66	0.598	118.2	2.59 2.58	313
	IV	80.32	0.588	137.7	3.05 ⁵ 3.04	317
	V	88.86	0.532	151.85	3.37 3.35	321
	VI	89.38	0.522	154.8	3.44 3.42	316.5

¹⁾ Cf. also H. KAMERLINGH ONNES and B. BECKMAN, Comm. N^o. 129a, Table VII.

²⁾ Cf. for instance W. MEISSNER, Ann. d. Phys. (4) 47 (14 Sept. 1915), p. 1001. [Added in the translation].

T is sufficient to calculate the temperatures from that calibration.

In Fig. 1¹⁾ the results of our measurements are represented. In the upper left-hand diagram the region up to 25° K. is represented on a larger scale.²⁾

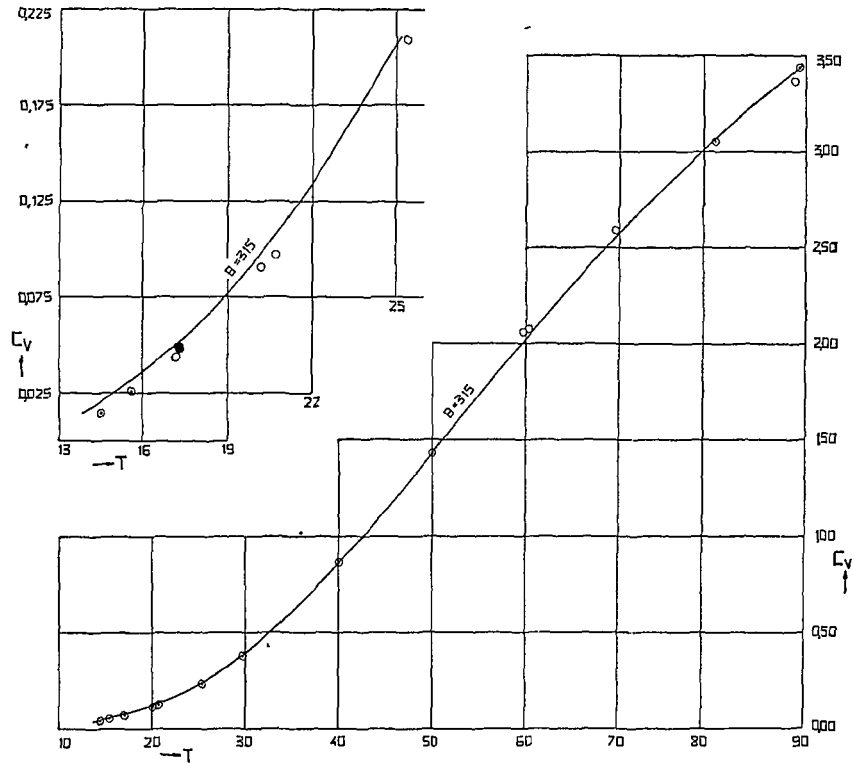


Fig. 1.

The curve has been calculated from DEBIJE's formula³⁾ with $\theta = 315$. DEBIJE's formula appears again to be capable of representing the atomic heat over a large region — the ratio of the largest to the smallest value of the measured atomic heats amounts to more than 80 — with a good approximation.

In table IV we have compared the atomic heats of copper in the region of the liquid hydrogen temperatures with the T^3 -law derived by DEBIJE for low temperatures:

$$C_v = 4641 \left(\frac{T}{\theta} \right)^3.$$

¹⁾ In Fig. 1 the vertical line which indicates $T = 80$ has been drawn inaccurately; it has to be moved 1.25 mm. to the right. [Note added in the translation].

²⁾ At 88° K. our results agree fairly well with those found by NERNST i.e., at the lower temperatures (33°–23° K.) our values are smaller

³⁾ P. DEBIJE. Ann. d. Phys. (4) 39 (1912), p 789.

TABLE IV. Copper.						
No.	T	C_v	θ	C_v calc. ($\theta = 325.1$)	Obs.—Calc.	
						in %
16 Dec. '14						
II	14.51	0.0396	329.6	0.0412	— 0.0016	—4.0
III	15.59 ⁵	506	326.3	512	— 6	—1.2
IV	17.17	687	324.6	684	+ 3	+0.4
V	20.19 ⁵	0.1155	321.1	0.1112 ⁵	+ 42 ⁵	+3.7
I	20.74 ⁵	1217	324.1	1206	+ 11	+0.9
			mean 325.1			

In these measurements, which are more accurate than those of July '14 (Comm. N^o. 143 § 6), a small deviation from the T^3 -law shows itself. The deviation is in the sense that at decreasing temperature the atomic heat *decreases more rapidly* than follows from the T^3 -law.

The deviation becomes still more apparent, if one compares the atomic heat over the whole region of the measurements of this paper with DEBYE's general formula for the atomic heat, cf. fig. 1 and the values of θ in table III.

In the liquid hydrogen region and above it, up to 40° K., the values of θ decrease continually (fig. 2). In this respect the

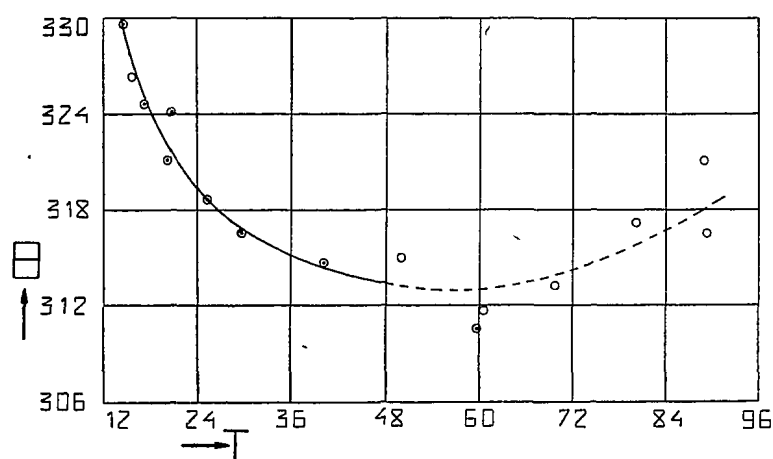


Fig. 2.

behaviour of copper differs from that of lead. For the latter metal the values of θ increase with increasing temperature in the liquid

hydrogen region, and begin to decrease beyond about 30° K.¹⁾

§ 4. Table V contains values of the energy U , which are derived

TABLE V. Copper.			
T	U in cal ₁₅ .	$\frac{U}{T}$	θ_u
20	0.557	0.0278 ⁵	322
30	2.86	0.0952	320
40	8.94	0.223	317
50	20.31	0.406	316 ⁵
60	37.8	0.629	315
70	61.1	0.873	314
80	89.4	1.118	314
90	121.7	1.352	315

¹⁾ Our results point further to an increase of θ for copper above 70° K. It is true, that the increase hardly exceeds the degree of accuracy reached in our measurements, but meanwhile it finds a confirmation in the results obtained by SCHIMPF, ZS. physik. Chem. 71 (1910), p. 257, by RICHARDS and JACKSON, ZS. physik. Chem. 70 (1910), p. 414, by KOREF, Ann. d. Phys. (4) 36 (1911), p. 49, R. EWALD Ann. d. Phys. (4) 44 (1914), p. 1213 and by ROLLA, Gazz. chim. 44 I (1914), p. 646, at temperatures between that of liquid air and room temperature or 0° C. respectively. A curve which is drawn through our results below 90° K., and which represents the observations mentioned above as follows:

Interval of Temperature	\bar{c}_p		Obs.—Calc.	
	from curve	observed		
83—290° K.	0.0790	0.0786	—0.0004	} SCHIMPF.
194—290	0.0879	0.0880	+ 1	
85—293	0.0794	0.0789	— 5	RICHARDS and JACKSON.
83.5—190	0.0710	0.0720	+ 10	} KOREF.
196.5—273.1	0.0873	0.0878	+ 5	
82.0—191.1	0.0708	0.0722	+ 14	} EWALD.
197.9—273.1	0.0874	0.0881	+ 7	
82—191.5	0.0709	0.0720	+ 11	} ROLLA.
198.2—273.1	0.0874	0.0860	— 14	

gives i. a. the following values of C_p :

by graphical integration from a curve which has been drawn through the experimental points of fig. 1, with an extrapolation below 14° K. on the basis of the assumption that the T^3 -law is the ultimate limiting law.

The last column gives the values θ_u calculated from $x = \frac{\theta_u}{T}$, x being derived from DEBIJE'S formula for the energy:

$$U = 9 Nk T \frac{1}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1}$$

The change of θ_u with T has the effect of making the values of θ , which are derived directly from the atomic heats, differ somewhat from those of θ_u .

For copper θ_u appears to decrease with increasing temperature in the region of 20 to 70° K., the rate of decrease being more rapid at the lower than at the higher temperatures of this region.

§ 5. The values of θ_u found in § 4 (and also those of θ , § 3) are smaller than those following from the formula given by DEBIJE l.c., which with the value found by MILLIKAN for the AVOGADRO number (cf. Suppl. N° 36b, March '14) changes to:

$$\theta = \frac{3,657 \cdot 10^{-3}}{M^{1/2} v^{1/2} \sigma^{1/2}} \frac{1}{[f(\sigma)]^{1/2}},$$

viz.: for 18° C.: $\theta = 333$, for -191° C.: $\theta = 344$ ¹⁾.

In LINDEMANN'S formula ²⁾:

$$\theta = k_L \frac{h}{k} \frac{T_s^{1/2}}{M^{1/2} v M^{1/3}}$$

one finds for Cu from $\theta = 315$: $k_L = 2.72 \cdot 10^{12}$
 whereas for Pb from $\theta = 88$ follows: $k_L = 2.81 \cdot 10^{12}$, where for v , the values at $T = 0,2 T_s$ have been used.

$$\begin{array}{ccccccc} T = & 120 & , & 160 & , & 200 & , & 240 & , & 280 & , \\ C_p = & 4.22 & , & 4.85 & , & 5.28 & , & 5.60 & , & 5.80^5 & , \text{ from which we find:} \\ \theta = & 331 & , & 343 & , & 336 & & & & & \end{array}$$

On the contrary the results of E. H. and EZER GRIFFITHS, Phil Trans. 214 A (1914), p. 319, cannot be reconciled so easily with ours as can be seen from the fact that they give: at 138° K. $\theta = 278$, at 149.5° K. $\theta = 285$

¹⁾ Calculated from: 18° C.: $\rho = 8,94$, $\kappa = 0.74 \cdot 10^{-12}$, $\sigma = 0,35$
 -191° C.: 9,12, 0,69 $\cdot 10^{-12}$, 0,35.

The value of κ at 18° C. has been taken from E. GRÜNEISEN Ann. d. Phys. (4) 25 (1908), p. 848, the change of ρ with temperature from E. GRÜNEISEN, Ann. d. Phys. (4) 33 (1910), p. 1264.

σ has been assumed to change inappreciably with the temperature according to E. GRÜNEISEN, Ann. d. Phys. (4) 33 (1910), p. 1272.

²⁾ F. A. LINDEMANN, Physik. ZS. 11 (1910), p. 609.

As LINDEMANN'S formula can be deduced¹⁾ from the principle of similarity, applied to solid substances, the data mentioned for k_L can serve at the same time as a comparison of these two metals with respect to that principle. In this comparison the change of θ with the temperature has, however, not been taken into account.

Physics. — "*Further experiments with liquid helium. O. On the measurement of very low temperatures. XXV. The determination of the temperatures which are obtained with liquid helium, especially in connection with measurements of the vapour-pressure of helium.*" By H. KAMERLINGH ONNES and SOPHUS WEBER. (Comm. 147*b* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction.* In this paper will be given some new determinations of vapour-pressures of helium based on more accurate temperature-measurements, as also a contribution to the knowledge of the correction for the thermal molecular pressure, which has to be applied with constant volume-thermometers for low temperatures with gas under diminished pressure, if the manometer is kept at the ordinary temperature.²⁾

This correction was discussed in Comm. 124*b* (Dec. 1911); an estimate of its magnitude, which was necessary to form a judgment of the value of the temperature-determinations, showed that its influence would only exceed the limits of accuracy then given, viz. 0.1 of a degree, in the measurement of the lowest temperatures.

The present determinations of the boiling point of helium made with the aid of a helium thermometer with mercury-manometer arranged for more accurate measurements have enabled us to test the accuracy of the temperature-determination in the previous series of experiments with liquid helium, in which this point had also been determined. It appears that the difference of the previous results from the present can be explained by the correction for the thermal molecular pressure. This correction remains below the value, then given for the limit of accuracy. As to the correction at the lowest temperatures which were measured, this also appears to have about the estimated magnitude. The previous measurements are thus as a whole confirmed.

¹⁾ H. KAMERLINGH ONNES, Comm. N^o. 123 (June '11).

²⁾ Compare for a different arrangement the conclusion of § 7, Comm. Suppl. 84 (Sept. 1913), where the investigation contained in the present communication was also announced.