## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

H. Kamerlingh Onnes & W.H. Keesom, The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80°K. and of copper between 15° and 22°K, in: KNAW, Proceedings, 17 III, 1914-1915, Amsterdam, 1915, pp. 894-914

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'

and only the slow automatic extension and flexion movement with a rhythm of  $2^{\circ}/_{\circ}$  per second remained visible, often during 30 seconds and longer.

All the records shown in this paper are obtained from the patellar tendon-reflex. Yet their significance is more general, as also other exaggerated deep reflexes sometimes show changes of a similar nature.

Physics. — "The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K." By W. H. KEESOM and H. KAMERLINGH ONNES. Communication N°. 143 from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of October 31, 1914).

§ 1. Introduction. Soon after the methods of obtaining baths of temperatures which are accurately known and can be kept constant for a long time, in the range between the boiling point and the melting point of hydrogen, had been worked on , in the errorgenic laboratory at Leiden, a series of investigations on the calorimetry at very low temperatures was started there. DEWAR's measurements on the mean specific heat of different substances between the temperature of liquid air and the boiling-point of hydrogen ') had particularly drawn attention to the interest of those investigations. The continuation of his experiments in the still lower region of temperatures mentioned above seemed very desirable '). As was done by DEWAR the series of investigations in this direction was begin by determinations of the heat of vaporisation of hydrogen. A report on the first results of those determinations was given at the Dutch

 $\cdot$ <sup>3</sup>) This was pointed out at the 1st International Congress of Refrigeration at Paris 1908. H. KAMERLINGH ONNES, La liquéfaction etc. Note J. Sur les expériences à faire aux températures très basses. Leiden Comm. Suppl. N<sup>0</sup>, 21*a* p. 29.

<sup>1)</sup> Cf. specially H. KAMERLINGH ONNES, Leiden Comm. No. Off (Proceedings Sept. '06) and H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Leiden Court. N. 1014 (Proceedings Dec. '07).

<sup>&</sup>lt;sup>2</sup>) J. DEWAR, Proc. Roy. Inst. March 25, 1904, Proc. Roy. Soc. A 76 (1905) p. 325, later more extensively between the boiling point of nitrogen and that of hydrogen: Proc. Roy. Soc. A. 89. (1913) p. 158.

Congress of Science and Medicine at Groningen (1911)<sup>1</sup>). An investigation regarding the specific heat of lead, after which other metals were to follow, at hydrogen temperatures, an investigation which had a particular interest with a view to EINSTEIN's theory and also in connection with <sup>2</sup>) NERNST's theorem, was announced on that occasion.

Since then in NERNST's laboratory a highly important series of investigations on the specific heat has been made by himself and by his collaborators <sup>3</sup>). In particular the investigations on solids at low temperatures, which had already been made down to the temperatures of liquid air boiling under reduced pressure, were continued to the temperatures which can be obtained with liquid hydrogen. Besides KAMERLINGH ONNES and HOLST<sup>4</sup>) made preliminary measurements of the specific heat of mercury at helium temperatures. The investigations mentioned have already furnished a great number of highly valuable data, which in particular have served for a test of the theories of DEBIJE<sup>5</sup>) and of BORN and v. KARMAN<sup>9</sup>). The method we followed is mainly that which has been developed by NERNST and EUCKEN. Notwithstanding all that the continuation of our programme seemed to remain desirable. First, when NERNST'S investigations had followed the specific heat down to the region of hydrogen temperatures, because only a few of his observations entered into this region and the accuracy of the observations left some doubt with NERNST himself, and later, when between the boiling point and the melting point of hydrogen also more accurate determinations had been made in his laboratory 7), because for the investigation of the questions which

 W. H. KEESOM. The heat of vaporisation of hydrogen. Handel. 13de Ned. Nat. en Geneesk. Congres, April 1911, p. 181 Published'also Leiden (Jomm N<sup>0</sup>.137e.
<sup>2</sup>) Cf. also H. KAMERLINGH ONNES. Reports of the IInd International Congress of Refrigeration. Vienna 1910 (Comm. Leiden Suppl. N<sup>0</sup>. 21b p. 42).

<sup>3</sup>) For the literature we refer to Leiden Comm. Suppl. N<sup>0</sup>. 23 "Die Zustandsgleichung" Math. Encycl. V. 10 Note 838. Later : A. EUCKEN and F. SCHWERS. Verh. d. D. phys. Ges. 15 (1913) p. 578, W. NERNST and F. SCHWERS. Berlin Akad. Sitz. Ber. 1914 p. 355. R. EWALD Ann. d. Phys. (4) 44 (1914) p. 1213.

4) H. KAMERLINGH ONNES and G. HOLST. Comm. Nº. 142c (Sept. '14).

1

<sup>5</sup>) P. DEBIJE. Ann. d. Phys. (4) 39 (1912), p. 789. W. NERNST and F. A. LINDEMANN Berlin Akad. Sitz. Ber. 1912, p. 1160. Cf. also W. NERNST, Vorträge Wolfskehl Congress Gottingen 1913, p. 61.

<sup>6</sup>) M. BORN and TH. v. KARMAN. Physik. ZS. 13 (1912), p. 297; 14 (1913), p. 15, 65. H. THIRRING, Physik. ZS 14 (1913), p. 867; 15 (1914), p. 127, 180. Cf. M. BORN, Ann. d. Phys. (4) 44 (1914), p. 605.

7) A part of our observations had already been made when the results of EUCKEN and SCHWERS were published (see § 5). The completion of even the limited part of the programme, which is contained in this communication, has been much retarded, partly by the wish to altain very trustworthy results.

13

- 3 -

have now come to the front a high degree of accuracy is desirable.

In this respect it was an advantage:  $1^{st}$  that particularly by the investigation of KAMERLINGE ONNES and HOLST<sup>1</sup>) on the scales of the hydrogen and the helium constant volume thermometers we could avail ourselves of a more accurate temperature scale<sup>2</sup>);  $2^{nd}$  that the cryostats used at Leiden allowed the measurements to be performed under more favourable circumstances in other respects also. In fact in the measurements published in this paper an accuracy of  $2^{\circ}/_{\circ}$  has been reached at hydrogen temperatures, while there is reason to expect that in subsequent measurements the accuracy will still be considerably increased.

§ 2. Method. Apparatus. We followed with some modifications the method which has been in particular developed by NERNST and EUCKEN, and which has shown itself to be very suitable for low temperatures. In this method a block of the metal to be investigated, provided with wires for heating and temperature measurement, is suspended in a vacuum which is made as perfect as possible. Within the block a measured quantity of heat is developed by an electric current, and the increase of temperature produced is measured.

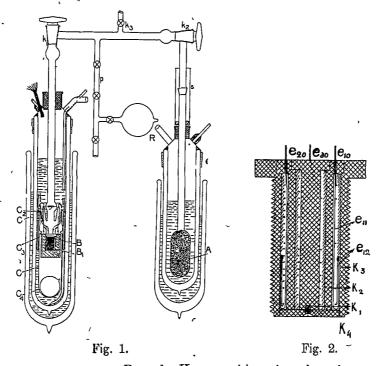
Fig. 1 represents the cryostat with the calorimeter. To protect the block against the residual heat radiation which enters the calorimeter vessel C (the vacuum-vessels are silvered a slit being left open), it is silvered on the outside up to a few mms. below the sealingplaces  $C_3$  of the platinum wires. Moreover the plate  $C_1$ , which through a platinum wire is in heat conducting connection with the bath, prevents radiation from above.

In the block B of the metal to be investigated a chamber has been drilled, into which the core K fits tightly. This core contains the wires which serve for heating and for measuring the temperature; when the temperature wire has once been calibrated and the heat capacity of the core measured separately, it can serve for the successive measurements of the specific heat of all the metals of of which suitable blocks can be made, and of other substances also when use is made of a suitable vessel. The core consists (Fig. 2) of a solid cylinder  $K_1$  and two cylindrical mantles  $K_2$  and  $K_3$ , all

<sup>1)</sup> H. KAMERLINGH ONNES and G. HOLST. Comm. No. 141a (May 1914).

<sup>&</sup>lt;sup>2</sup>) The temperature scale used by NERNST, and also those of EUCKEN and SCHWERS and of NERNST and SCHWERS are mainly based upon the older calibration of the thermometer  $Pi_1$  by KAMERLINGH ONNES, BRAAK and CLAY, which has to be replaced by the newer one of KAMERLINGH ONNES and HOLST. Cf. further § 3.

of copper, provided above with flat, tightly fitting collars, and of a copper plate  $K_4$ , which is in addition connected with  $K_1$  by means



of a copper screw. Round  $K_1$  a gold wire has been wound doubled on itself; for insulation and at the same time for heat conduction enamel and thin paper were used; the electrodes  $e_{10}, \ldots e_{40}$ , stout platinum wires (1,5 mm.), which are led through the collars and insulated from these, and protrude outside the core, are rolled out below to flat bands which are a few centimeters longer than the cylinder; to the ends of these the gold wire is soldered with gold, after which the band was bent up  $(e_{13} \ldots)$  and fastened to the core and insulated.

The space which remained within  $K_2$  was filled up with the copper-tin-amalgam which is used in dentistry. In the same way a constant wire was wound round  $K_2$  and enclosed between  $K_2$  and  $K_3$ . Then the whole was closed by the plate  $K_4$  below, and the different parts were united as much as possible by Wood-metal. The insulation was tested with an insulation meter and found to be more than sufficient.

The block B is suspended from two platinum wires (0.6 mm.) with the aid of two small glass rings. These platinum wires serve at the same time for conduction of the heating current. They are therefore connected to the electrodes of the constantin wires by platinum wires (0,2 mm.). For simplicity the wires, which serve for measuring

- 5 -

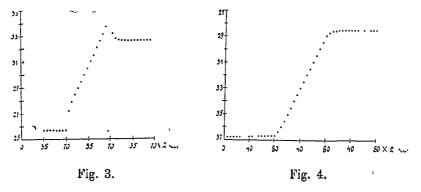
the potential difference between the electrodes  $e_{10}$ ,  $e_{20}$  of the constantin wire, are applied outside the calorimeter vessel near the sealing places. The resistance between these junctions and the ends of the constantin wire is inappreciable compared with the resistance of the latter (140  $\Omega$ ). For the gold wire, which serves as a thermo-

meter, potential as well as current wires (within the calorimeter vessel 0.1 mm. platinum, insulated with silk) lead directly to the electrodes.

The stopcocks  $k_1$  and  $k_2$  have wide borings,  $k_3$  leads to a GAEDE mercury pump, which serves for evacuating the charcoal and for a preliminary evacuation of the calorimeter vessel, and to a Mc.-Leod gauge, R is a reservoir which is filled with hydrogen; with the aid of the pipette p a quantity of this hydrogen is admitted into the calorimeter vessel when it is required to bring about heat conduction between the block and the bath.

The charcoal tube A, made of glazed opaque quartz, was filled with cocoa-nut charcoal, and evacuated for a sufficient time at 600° C. before each series of measurements. During the measurements it is cooled with liquid hydrogen.

To diminish the exchange of heat between the metal block and the bath through the conducting wires, during the measurements the bath that surrounds the calorimeter was brought as nearly as possible to the temperature at which the measurement was to be made. The time-rate of the temperature before the heating and after the heating, at least after a few tens of seconds, was as a rule very small, if not inappreciable. For illustration in Fig. 3 and 4



the time-curve of the galvanometer, which indicates the temperature, during two measurements is represented, viz. for a measurement of the specific heat of lead (Fig. 3) and for a measurement of the specific heat of copper (Fig. 4), respectively. The increase of temperature was in both cases about 1 degree. In the measurement with lead the temperature of the core appears to have risen about 1/s degree above the mean temperature of the lead block during the heating, in the measurement with copper, for which the heat supply per second was chosen smaller in accordance with the smaller specific heat, the corresponding temperature difference is not appreciable. Where necessary, corrections for the heat exchange with the bath were applied.

The heat supply. The arrangement for sending a current of measured intensity and potential difference during a definite time through the constant heating wire is represented in Fig. 5 together with the arrangement  $^{1}$ ) for measuring the resistance of the gold thermo-

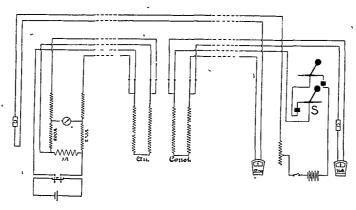
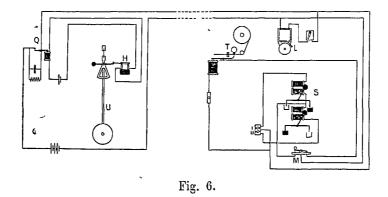


Fig. 5.

meter wire. Intensity and potential difference were read on accurate WESTON millivolt- and voltmeters. These were calibrated repeatedly for the measuring ranges used with the aid of a standard element of the WESTON Cy., standard resistances and a compensation apparatus free from thermoelectric forces with an auxiliary apparatus according to DIESSELHORST, all calibrated at the Physikalisch Technische Reichs-



<sup>1</sup>) In the figure the regulating resistance and the milli-ampèremeter between accumulator and commutator have been omitted.

anstalt. The switch S for closing and opening the current served for measuring off the time. Fig. 6 represents the complete arrangement<sup>1</sup>) for measuring off and registering the time. The clock U with second pendulum, provided with a HOHWU registering arrangement H,

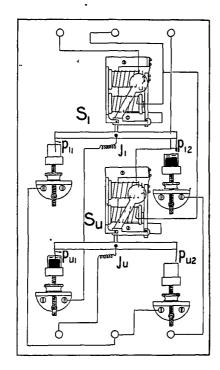


Fig. 7.

closes, respectively opens in passing its equilibrium position a current which operates a relais Q. This closes, respectively opens a current, which makes the bell L give a stroke every two seconds; this is registered by the telegraphic apparatus T the Morse-key M being in its position of rest. If, after contact has been made at i by a plug, M is pressed down at a moment that no current goes through (to be recognized from the position of the tongue of the bell), at the next closing of the current by the relais the beam  $j_i$  of the contact-key  $S_i$  (see Fig. 7) will be released, the platinum wire  $p_{i_2}$  will fall into the mercury, and the heating current through the constantin wire will be closed <sup>2</sup>). The switching out is operated in the same way by  $S_{\mu}$ 

the contact plug having been transferred from i to u. As a control the moments of switching in and out are registered by T (Fig. 6) through the corresponding dash on the paper strip being absent.

An accuracy of 1/10 of a second is certainly attained with this arrangement.

The temperature measurement. The scale of the gold resistance thermometer is dealt with in § 3. In Fig. 6 the Thomson bridge

<sup>&</sup>lt;sup>1</sup>) This arrangement was already used in the determination<sup>i</sup> of the heat of vaporisation of hydrogen, cf. Comm. N<sup>6</sup>. 137*e*.

<sup>&</sup>lt;sup>2</sup>) The distances of the points of  $p_{i_3}$  and  $p_{u_1}$  (fig. 7) above, and below the respective mercury surfaces (covered with paraffin oil partly for suppressing the opening spark) are small and are made equal to each other by adjusting the mercury cups, whereas the velocity of fall of the two beams  $j_i$  and  $j_u$  was also made as equal as possible. The two other cups (see  $p_{i1}$  and  $p_{u2}$ ) may serve to use the apparatus as a switch-over key (e.g. if the same wire has to be used as a heating and as a thermometer wire, cf. § 3 at the end); in the present experiments they were not filled with mercury.

for the measurement of the resistance is also represented. The galvanometer was of the DIESSELHORST type with a period (undamped) of 4 sec. Before a calorimetric determination the resistance was measured, and the deflection of the galvanometer for a definite change in the ratio of the branches in the THOMSON bridge, the "sensitivity", determined. Then with a definite ratio of the branches the movement of the galvanometer (Fig. 3 and 4) was followed during the experiment. After this the measurements of the resistance and of the sensitivity were repeated. The current for measuring the resistance was 5 milliamperes. The heating current was for the lead 30 tot 50, for the copper 12 to 27 milliamperes. Considering the ratio between the resistances of the thermometer and the heating wires the development of heat in the temperature measurement does not come into account.

We gladly record our cordial thanks to Dr. G. HOLST and Mr. P. G. CATH for the aid they afforded us in undertaking the temperature measurements.

Account had to be taken of the circumstance, that the reduction factor, which gives the ratio between the galvanometer current in the THOMSON bridge and the difference between the measured resistance and the resistance which would give no deflection, depends on the resistance in the variable branches of the bridge. A correction for this was always applied.

§ 3: The resistance thermometer. For the resistance thermometer a gold wire was chosen, as in the 'range of the measurements  $(14-90^{\circ} \text{ K.})$  gold is more suitable for interpolation than platinum '), and as on the other hand the indications of the gold thermometer are constant, if it is suitably treated before use (glowing before winding, then repeatedly cooling in liquid hydrogen and returning to room temperature'. Before each series of measurements the constancy of the resistance of the wire was tested by a measurement at the boiling point of hydrogen.

In the temperature range of liquid hydrogen the gold thermometer was calibrated with the aid of a hydrogen vapour pressure apparatus as used in Comm. N<sup>0</sup>. 137*d*. The temperatures were deduced from formula (1) of that paper. In this way the scale of the gold thermometer is reduced to that of  $Pt_{I'}$ , which has been once more accurately fixed by the research of KAMERLINGH ONNES and HOLST (Comm. N<sup>0</sup>. 141*a*). In the range of liquid oxygen this was done with the aid

14

<sup>1)</sup> H. KAMERLINGH ONNES and G. HOLST. Comm. No. 142a (June 1914).

of auxiliary thermometers of platinum and of gold which had been compared directly with  $Pt_{I'}$ .

The data for the gold thermometer  $Au_{\iota_1}$ ), which was used in the measurements of May –June 1913 (table IV), were inserted in Comm. N°. 142*a* § 4*e*. Table I contains the data for the gold thermometer  $Au_{\iota_3}$ , which was used in June—July 1914.

Т	Resis	tance of $Au_{c_3}^{(2)}$		Resistance of constantin
		W-R <sub>I</sub>	W-R <sub>II</sub>	Const. c3
14.16°K.	0.6148	0.00	0.00	136.621
15.79	6286	— 10	+ 1	918
17.00	6419	- 14	0	13 <b>7</b> .138
17.96	6542	- 14	0	312
19.35	6749	- 8	0	565
20.31	6911	0	0	743
20.48 ·	6946	— 0 <sup>5</sup>	- 3	776
68.22	2.6093			143.388
78 28	3.0917			144.000
90.27	3.6549			656

TABLE I.

We also communicate in table II the calibration data of a gold thermometer  $Au_{c_{2}}$ , which became defective in some measurements concerning the specific heat of aluminium.

In connection with a remark by ZERNIKE in a paper published in these Proceedings, viz. that the resistance of  $Au_{c_1}(\text{Comm. N}^\circ. 142a \$ 4e)$ for the range of hydrogen temperatures can be represented fairly accurately by a formula

we have inserted under  $W - R_{I'}$  in the tables I and II the differences between the observed temperatures and those calculated from the resistances with the formulae:

$$W = 0.5912 + 5.871.10^{-7} \cdot T^{4}$$
 (Au<sub>c3</sub>) . . (2a)

$$W = 0.07279 + 1.0974 \cdot 10^{-7} \cdot T^{4} \quad (Au_{cs}) \quad . \quad (2b)$$

In Fig. 8 we have represented besides these deviations (indicated by squares and triangles respectively), also those of  $Au_{c_1}$  (indicated by circles), for which T was calculated from

1) Wire of 0.05 mm. of HERAEUS.

<sup>2</sup>) Wire of 0.1 mm. furnished in January 1914 by HERAEUS.

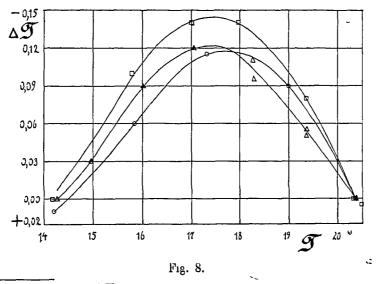
ĥ	AA.	
u	MY.	
v	$\mathbf{v}\mathbf{v}$	

•

~

TABLE II.

		<u> </u>	TABLE II.	••••••••••••••••••••••••••••••••••••••	
		R	esistance-of Au	, <sup>1</sup> )	
N	р. к	Т	Resistance	W—R <sub>I</sub>	
		In liquid hy vapour press	drogen with ure apparatùs	•	
9 Dec	'13 II	14.25	0.077315	0.00	
	m	14.95	7831	— 3	1
	IV	16.02	8019	- 9	
	v	17.05	8232	— 12	
	VI	18.01	8461	— 11	
8 Dec.	I	18.04	8466	95	
9 » _	VIIa	19.36	8838	5	much liquid in vapour
	b	19.365	88395	55	little , apparat.
	VIII	20 36	9165	0	
		in liquid oxy	gen with $Pt_{I'}$		
16 Dec.	IV	59,00	0.4392		
	ш	77.84	6552		
15 »	II	86.41	7517		
16 🔹	II	86.43	7519		
15 »	I	90 20	7941		
16 »	I	90 30	7962		



1) Wire of 0.1 mm. of HERAEUS.

ll

•

• >

904

## $\dot{W} = 0.2691 + 5.425 \cdot 10^{-7} \, \dot{T}^{4} \qquad (Au_{c_{l}}) \, . \, . \, . \, (2c)$

11.2

These deviations are certainly not large (at most rather more than 0.1 degree); they are, however, appreciably larger than the inaccuracy of the measurements. They are on the whole larger as the impurity of the wire (as estimated by the ratio  $\frac{a}{b}$ ) increases. This increase of the deviations with increasing impurity seems, however, not to be strong enough to warrant the conclusion, that for pure gold proportionality of the resistance with  $T^4$  within the limits of the accuracy of the measurements would exist in the hydrogen region. This will find its expression in ZERNIKE's more general interpolation formula in the fact, that in this range the coefficients of the polynomial in the denominator already make their influence felt. GRÜNEISEN's relation  $W - C_p T$  brings this in connection with the deviation which the specific heat of gold shows in this range from the  $T^*$ -law<sup>1</sup>).

In table I under  $W - R_{II}$  we have also inserted the deviations between the observed temperatures and those calculated from the formula:

 $W = 0.6879 - 0.01741 T + 0.000865 T^{2}. \quad (Au_{c_{3}}) \quad . \quad (3)$ 

Practically this formula represents the resistance of  $Au_{c_3}$  accurately in this range, so that in the hydrogen range dW/dT depends linearly on T. Outside this range the formula would lead, however, to quite incorrect values<sup>2</sup>).

For the calculation of the results of the calorimetric determinations dealt with in this paper graphic interpolation was made use of. For the hydrogen range graphs of W and of  $\Delta W/\Delta T$  were made on a sufficiently large scale according to the observed values. For the higher temperatures T and dW/dT were taken from graphs for the whole range of the calibration; for that purpose the W-curve was first drawn, from this values of dW/dT were taken for a

<sup>1</sup>)  $8^{0}/_{0}$  at 20° K. if for gold  $\theta = 166$  is assumed according to DEBIJE.

<sup>9</sup>) We have also investigated whether the resistances of  $Au_{c_3}$  and  $Au_{c_1}$  (of which the first mentioned was enclosed in enamel, the second in paraffin) can be reduced to each other, either with the linear relation, which according to NERNST, or with the quadratic one, which according to HENNING exists between the values of the resistances of those wires corresponding to the same temperature. We found, however, that in the range from 14° to 90° K. both relations give deviations of several tenths of a degree between calculation and observation. The same result as regards NERNST's rule was found recently by H SCHIMANK, Ann. d. Phys. (4) 45 (1914), p. 706. As regards the exceptional difference between observation and calculation in the case of  $Au_{VI}$  which was found by this physicist, we refer to the erratum given in Suppl. N<sup>0</sup>. 19 (May 1908): in Comm. N<sup>0</sup>. 99c p. 22 table I column  $Au_{VI}$  for 0.16822 is to be read 0.25234.

number of points in the range between hydrogen and oxygen temperatures, and these values were then smoothed graphically in the dW/dT-figure.

Together with the gold wire we accurately calibrated each time the constantin wire which was to serve for the heating, in order that this wire might serve as thermometer also (cf. p. 904 note 2) in case the gold wire should become defective. The corresponding data are given in Comm. N<sup>o</sup>. 142 $a \leq 4d$  and in this paper table I.

<u>    No.</u>	Mean temperature	Increase of temperature	Heat capacity in Joules /_degree						
10 June II	14.61° K.	0.763	0.727						
III	15.28	1.123	0.785						
IV	16.19	. 0.992	. 0.887						
v	17.37	1.149	1.019						
VI	18.285	0.964	1.155						
VII	19.115	0.867	1.288						
I	20.105	1.288	1.530						
VIII	20.16	1.048	1.406						
IX .	21.13	0.938	1.565						
X*.1)	28.375	0.979	2.99						
XI* -	29.00 _	0.927	3.17						
XII	36.40	0.675	5,04 -						
XIII*	46.32	0.509	8.19						
13 June II*	61.87	0.503	- 12.91						
III*-	62.16	0.490	13.22						
IV	70.33	0.429	15,39						
~ v	70.745	0.417	15.58						
I*	80 36	0.346	18.74						
14 June I	80.515	0.318	17.87						
II	80.88	0.356	18.56						

§ 4. Heat capacity of the core. This was measured separately in TABLE III.

 For the measurements marked by an \* the calculation of the increase of 60
Proceedings Royal Acad. Amsterdam. Vol. XVII. the same way as described in the preceding % for the block of metal and core together. We only communicate the results of the measurements for the core  $K_{III}$  which served for the measurements of June/July 1914 (table III).

§ 5. Lead. With lead ("KAHLBAUM") 3 series of measurements were made. The results of the first two series (1913) have been united in table IV, that of the last series (1914) in table V. Weight of the lead block: for the measurements of table IV: 715,6 grammes, for those of table V (the same block after removal of a layer at the surface) 709.7 grammes.

,	The	measurements	of	1914	must	be	considered	as	more	accurate	
1				Т	ABLE	IV	•				

Atomic heat of lead							
No.		Mean temperature	Increase of temperature	Heat capacity block + core in Joules/degree	id. core	Atomic heat in cal. <sub>15</sub> $C_p = C_v$	
16 May '13	II	14.96° K.	0.66	23 79	0.28	1.62	
	ш	15.86	0. <b>73</b> 5	27.27	0.33	1.86	
	IV	16.625	0.67	29.75	0.37	2.03	
	v	17 38	0.81	31.37	0.42	2 14	
	VI	18.19	0.73 <sup>5</sup>	33.85	0.49	2.30	
	VII	18.98	0.845	35 46	0.58	2.41	
	VIII	19.81	0.805	37 20	0 69	2.52	
5 June '13	I	15.00 🛫	0.735	24.73	0.29	1.69	
	II	15.71	0.795	27.11	0.32	1.85	
	III	16.43	0,71	30.37	0.36	2.07	
	IV	17.22	0.84	31 58 _	0.41	2.15	
	v	18.16	0 78	34.73	0.49	2.36	
	VI	19.10	0.95	36.68	0.59	2.49	
	VII	20 105	0.95	36.78	0.74	2.49	

temperature was not based on the determinations of the sensitivity (§ 2) immediately before and after those measurements, as in this case irregularities appeared to have occurred which have not yet been explained, but on an average value of the sensitivity, which was deduced for a number of successive measurements to which these belong. Apart from these irregularities the individual values for the sensitivity in one series of measurements did not differ as a rule by more than 2 to  $4^0/_0$  (occasionally by 6  $0/_0$ ).

than those of 1913. Nevertheless the latter are also communicated, as they confirm the conclusions to be drawn from the others.

 $\underbrace{C_o}_{v}$  was derived from  $C_p$  with the aid of the relation given by NERNST ') for lead.

$$C_p - C_r = 3,2 \cdot 10^{-5} T C_p^2.$$

In fig. 9  $C_o$  is represented according to the observations of 1914; fig. 10 gives a representation for the range of the hydrogen tem\_

TABLE V.
----------

Atomic heat of lead.							
, No.		Mean temperature	Increase of temperature	5 Din Heat grad transformed to the second se		Atomic heat in cal. <sub>15</sub>	
		temperature	Incr temp	core in Joules/degree	C <sub>p</sub>	C <sub>v</sub>	
23 June '1	4 XIV	14.19° K.	1.106	23.08	1.56	1.56	85.7
	Ш	15.315	0.927	26.83	1.815	1.815	85.9
	IV	16.275	0.9805	29.42	199	1.99	86.6
	V	17.24	1.001	32,18	2.17	2.17	86.9
	VI	18.255	1.008	35.72	2.41	2.41	86.3
	VII	19.27	1.054	37.56	2.53	2.53	88.2
	VIII	20 305	1.073	39 57	2.66	2.66	89.5
	II	22.31	0.962	44.58	2.98	2.97	89.9
	IX	27 51	1.019	54.41	3.60	3.59	92.4
	х	28.50	0.993	55.52	3.66	3.65	94.05
	XI	36.49 <sup>5</sup>	1.061	69.33	4.47	4.45	90.5
	XII	45.61 <sup>5</sup>	0.469	77.53	4.85	4.81	
	XIII-	46.25	0.907	80.50	5.04	5.00	87.9
24 June	I	57.20	0.476	89.47	5.43	5.38	
	II	58 00	0.804	88.93	5.37	5.32	88.5
-	111	69.28	0 676	92.19	5.37	5.31	
	IV	69.97	0.723	92.82	5.40	5.34	
Ň	V*1)	80.365	0.661	101.07	5.77	5.70	
	Vl*	80.86 <sup>5</sup>	0.671	99.82	5.67	5.60	90 1

<sup>1</sup>) W. NERNST. Ann. d. Phys. (4) 36 (1914), p. 426.

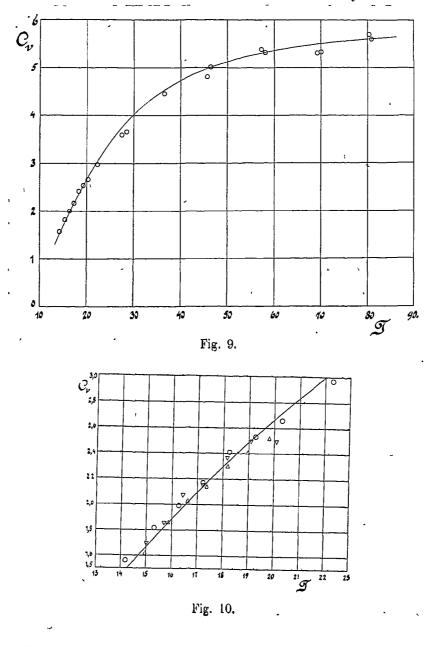
ł

60\*

12

peratures separately, the observations of 1913 ( $\Delta\Delta$  and  $\nabla\nabla$ ) being also included.

In these figures the curve, which according to DEBIJE represents the atomic heat, calculated with  $\theta = 88$ , which value was derived by EUCKEN and Schwers from their measurements on lead, is also represented. In agreement with EUCKEN and Schwers we find that the observations show a good concordance with DEBIJE's formula over the whole range. This concordance is, however, not complete; deviations show themselves which exceed the uncertainty of the results



- 16 -

of the observations <sup>1</sup>). This appears to be the case in the first place in the range of hydrogen temperatures : the curve which unites the experimental results crosses the curve calculated according to DEBIJE (Fig. 10), in such a way that at 14° K. the specific heat is greater, at 20° K. it is smaller than the value calculated with  $\theta = 88$ . These deviations continue in the lower part of the range between hydrogen and oxygen temperatures, and decrease again in the higher part. It is true that the drawing of a conclusion is made uncertain in this region by the interpolation, which the gold thermometer requires there. We do not, however, consider it probable, that the deviations in this region are to be ascribed to the inaccuracy of the interpolation: 1: as they are a regular continuation of the deviations in the hydrogen region which are established with certainty, 2. as there are no indications that the deviations have a different sign in one part of the region of interpolation than in the other, as would have been the consequence of an inaccurate interpolation with the method of interpolation used (§ 3).

We are therefore led to the conclusion that the specific heat of lead shows deviations from the curve calculated according to DEBIJE, which unites the determinations at oxygen and at hydrogen temperatures in the best possible way ( $\theta = 88$ ), in the intermediate range of the temperatures, to the extent of about  $4^{\circ}/_{\circ}$  at 30° K. (cf. also table VI).

These deviations may presumably find their explanation in one or more of the following circumstances: a. that we did not observe with a homogeneous substance crystallized in the regular system, but with a micro-crystalline aggregate consisting of different phases, such as the two different states of crystallisation assumed in supraconductors for the explanation of the micro-residual resistance (Comm. N<sup>o</sup>. 133 § 11), which perhaps also come into play in the experiments of COHEN and HELDERMAN<sup>2</sup>), who on the ground of their investigations assume, that with lead we are dealing with a metastable complex of two or more modifications, b that the approximate suppositions concerning the elastic spectrum made in DEBLIE's theory

1

<sup>2</sup>, E. COHEN, These Proc. June 1914, p. 200; E. COHEN and HELDERMAN, These Proc. Nov. '14, p. 822. COHEN 1. c. quoles measurements of LE VERRIER according to which at 220 to 250° C. lead would pass into another modification with appreciably larger specific heat (at constant pressure). The measurements by P. Schübel, Zs. f. anorg. Chem. 87 (1914), p. 81, do not, however, confirm this result.

<sup>1)</sup> At the points T = 57.20, 69.28 and 69.97 the inegularities mentioned m note 1 p. 905 in the determination of the sensitivity have presumably also occurred, though in a less degree. The first point has probably been calculated with too large the last two with too small a value for the sensitivity.

are not strictly valid, c. in a change with the temperature of the quantity  $\theta$  which occurs in that theory, in other words of the elastic properties of the material <sup>1</sup>).

Concerning b it may be remarked that for a substance which should crystallize in the simplest cubical space-lattice THIRRING has derived an expression for the specific heat from the theory of BORN and v. KÁRMÁN which in consequence of the more rigorous consideration of the molecular structure followed in this theory might give a nearer approximation to the actual conditions. It is true that for a thorough discussion in connection with THIRRING's deductions the data about the elastic constants in the temperature region considered are as yet wanting. Without these we can, however, establish the following facts. In table VI are given besides the deviations (W-R<sub>D</sub>) between the

	· · · · · · · · · · · · · · · · · · ·	IADLE VI.		<u>с</u>
T	$C_v$ ·		$ \begin{array}{c} \mathcal{W} - \mathcal{R}_{Th_1} \\ (\vartheta_{Th_1} = 67.5) \\ \vdots \end{array} $	$W - R_{Th_2}$ ( ${}^{\theta}_{Th_2} = 68$ )
14.19	1.56	+ 0.085		
15.315	1.815	+ 85		ę (
16.275	1.99 ·	+ 6		
17.24	2.17	+ 5	+ 0.26	
18.255	2.41	+ 8	+ 28	
19.27	2.53	0	+ 19	
20.30 <sup>5</sup>	2.66	- 7	+ 11	
22.31	2.97	75	+ 4	
27.51 .	3.59	15	- 10	ι ι
28.50	3.65	20	- ,16	- 0.20
36.495	4.45	- 8 /	~ _ 7	- 7
46.25	5.00	0	0	+ 1
58.00	5.32	- 1	1	- 1

TABLE VI	
----------	--

observed values of  $C_v$  and those calculated according to DEBIJE with  $\theta = 88$ , also the deviations  $W - R_{Th_1}$ , between the observations and the values calculated from a series given by THIRRING:

<sup>1</sup>) In determining this influence it should be borne in mind that, as is specially pointed out by EUCKEN, Verh. d. D. physik. Ges. 15 (1913), p. 571, the elastic properties must have been measured on homogeneous crystalline material.

$$C_{o} = 3R \left\{ 1 - \frac{B_{2}}{2!} \left( \frac{\theta_{Th}}{T} \right)^{2} + 3 \frac{B_{4}}{4!} \left( \frac{\theta_{Th}}{T} \right)^{4} - 5 \frac{B_{s}}{6!} \left( \frac{\theta_{Th}}{T} \right)^{6} \dots \right\}, \dots \left\{ 4 \right\}$$

in which  $B_1, B_2, \ldots$  are the Bernouillian coefficients and  $\theta_{Th}$  is a constant. Apparently the agreement of the observations with DEBIJE's formula is closer than that with this series of THIRRING.

It deserves further to be noticed, that this series can only be derived from the theory of BORN and v. KARMAN by the introduction of imaginary values for the elastic constants (assuming that they are independent of the temperature). From the series which THIRRING derives from the theory mentioned above :

$$C_{v} = 3R \left\{ 1 - \frac{B_{2}}{2!} J_{1} \left( \frac{h}{kT} \right)^{2} + 3 \frac{B_{4}}{4!} J_{2} \left( \frac{h}{kT} \right)^{4} \dots \right\}; \quad . \quad (5)$$

where  $J_1, J_2 \dots J_4$  represent definite functions 1) of the elastic constants  $c_{11}, c_{44}, c_{12}$  introduced by Voigt, the following series may be derived as the one which at the higher temperatures approaches nearest to series  $(4)^2$ :

$$C_{v} = 3R \left\{ 1 - \frac{B_{2}}{2!} \left( \frac{\theta_{Th}}{T} \right)^{s} + 1.1 \cdot 3 \frac{B_{4}}{4!} \left( \frac{\theta_{Th}}{T} \right)^{4} - 1.278 \cdot 5 \frac{B_{6}}{6!} \left( \frac{\theta_{Th}}{T} \right)^{6} + 1.6393 \cdot 7 \frac{B_{8}}{8!} \left( \frac{\theta_{Th}}{T} \right)^{8} \dots \right\}$$
(6)

Under  $W = R_{Th_2}$  in table VI are given the deviations between the observations and the values calculated from (6) with  $\theta_{Th_2} = 68$ . It appears that THIRRING's formula (5) with the special assumptions concerning the elastic constants for which it passes into (6), in the region for which the coefficients have been developed by him, practically coincides with DEBIJE's formula. Whereas, when the elastic constants do not agree with those assumptions, THIRRING'S formula deviates from DEBIJE's formula in a direction opposite to the observations.

Hence we come to the conclusion that a closer consideration of the molecular structure in the sense in which it is done in the theories of Born and v. KARMAN and of THIRRING, at least on the assumption of the arrangement in the simplest cubic space-lattice, does not account for the deviations indicated above.

It remains either to consider an arrangement in one of the other space-lattices of the regular system<sup>3</sup>), or to assume that one or both of the

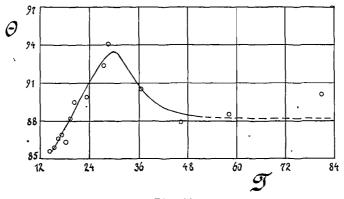
ł

1) H. THIRRING, Physik. Z. S. 14 (1913), p. 870 and 15 (1914), p. 181 note 1.

<sup>2</sup>) This would require  $c_{11} = \frac{3}{2}c_{44}$ ,  $c_{12} = 0$ . <sup>3</sup>) A comparison with the deduction by BORN, Ann. d. Phys. (4) 44 (1914), p. 607 of  $C_v$  for the space-lattice as deduced by BRAGG for diamond (also a regular crystal) leads, however, to quite analogous results as are given above for the simplest cubic space-lattice.

circumstances mentioned above under a and c also play a part 1). The latter of these, viz. a change of the elastic properties with the temperature, would be connected with deviations from the linear relation between the forces between the molecules and their relative displacements, which deviations DEBIJE<sup>2</sup>) also makes responsible for the thermal expansion.

In table V are given the values of O, which are obtained by applying DEBIJE's formula for  $C_v$  to the individual observations. They are united in Fig. 11<sup>3</sup>)<sup>4</sup>.



, I (10



§ 6. Copper. With copper we were as yet only able to make a series of measurements between 15 and 22° K. The copper was electrolytic copper of FELTEN and GUILLAUME, 596,0 grammes.

 $\overline{C}_{\mu}$  in table VII represents the mean atomic heat between the initial and final temperatures; for correction to the "true" atomic

<sup>1</sup>) Regarding  $\alpha$  it may still be remarked that the presence of a second modification of appreciably different properties in a considerable quantity would lead us to expect much larger deviations from DEBIJE's formula than appear actually to exist. If the circumstance mentioned under  $\alpha$  plays a part, we therefore have to assume a small quantity of a second modification, or a second modification whose elastic properties are only little different from those of the first.

<sup>2</sup>) P. DEBIJE, Vorträge Wolfskehlcongres Göttingen 1913.

<sup>3</sup>) The slow change, which EUCKEN and SCHWERS l.c. observed in the values of  $\theta$  for lead as derived from their measurements, and which does not coincide with that found by us, is considered by them as probably due to the uncertainty of the temperature coefficient of their resistance thermometer.

<sup>1</sup>) Fig. 11 gives a special illustration of the character of the deviations from DEBUE's formula over the whole range, and can also serve to calculate a smoothed value of  $C_0$  by reading the value of  $\theta$  corresponding to a definite T from the smoothed curve. At the same time it should be remarked, that the values of  $\theta$  represented in Fig. 11 do not coincide with  $h_{vmax}/k$ , if  $v_{max}$ , the maximum frequency according to DEBUE, changes with T.

heat  $C_{\rho} = C_{\nu}$  corresponding to the mean temperature of the measurement use-was made of the proportionality  $C_{\nu} - T^{3}$ , which appears to be valid in this region.

Table VIII contains the comparison of the experimental values

Atomic heat of copper.									
N°.	mean	increase of temperature	heat capacity copperblock core	Atomic heat in cal <sub>15</sub> .					
temp.		temperature	in Joules/degree.	<u>Ē</u> p	$C_p = C_v$				
3 July '14									
II	15.24° K.	4.222	2.748	0.0500	0.0491				
III	17.50	<sup>-</sup> 0.920	3.895	726	726				
IV	18.03	0.842	4.222	792	792				
v	18.89	0.726	4.884	930	930				
VI	19.58	0.606	5.305	1010	1010				
VII	20 88	1.355	6.417	1248	1247				
I	21.505	2.156	7.159	1414	1410				

TABLE VII.

TABLE VIII.

Atomic heat of copper.									
			с.		Obs.—C	alc.			
T	C <sub>v</sub>	θ	$C_{vcalc.}$ ( $\theta = 323.5$ )			in %			
15.24	0.0491	322.3	0.0486	+ 0.	0005	+ 1.0			
17.50	726	324.9	735	—	9	- 1.2			
18.03	792	325.2	804	-	12	- 1.5			
18.89	930	322.9	925	+	5	+0.5			
19.58	1010	325.6	1030		20	- 1.9			
20.88	1247	323.7	1249		2	- 0.2			
21.505	1410	320.0	1365	+	45	+ 3.3			
1		mean 323.5							

ł

ł

٤.

with the relation given by DEBIJE for sufficiently low temperatures :

 $C_v$ 

= 77,94 . 3 
$$R\left(\frac{T}{\theta}\right)^3$$
 . . . . .

(7)

The column headed  $\theta$  contains the values of  $\theta$  calculated according to formula (7) from the individual measurements.

From these measurements the conclusion can be drawn, that in the temperature range from 15 to 22° K. the specific heat of copper follows DEBIJE's  $T^{3}$  law within 2  $^{\circ}/_{0}^{-1}$ ).

## **Anatomy.** — "A case of occlusion of the arteria cerebelli posterior inferior." By Prof. C. WINKLER.

(Communicated in the meeting of November 28, 1914).

J. P., aged 58, artisan-painter, has never before shown any other irregularities but palpitations after physical exertion before the beginning of his illness on October 20<sup>th</sup> 1912.

At the age of twelve he became an apprentice painter, and always afterwards kept to this handicraft. As a young man he used to smoke much, and also drank much beer, but he firmly denies any sort of veneric infection, though he underwent a treatment for strictura urethrae at the age of 45 His father died of consumption, his mother of jaundice. The eldest *sister* died of apoplexy. The patient is the sixth among nine children. He married young and has five healthy children.

At eight o'clock in the morning of the  $20^{th}$  October he suddenly complained of dizziness and was obliged to sit down on a chair. He did not lose consciousness, but could no longer walk because his right leg had become lax. He could neither speak nor swallow, and suffered of double vision.

Before the beginning of this attack he had walked for a quarter of an hour over hilly ground, and for the rest had even kept himself unusually quiet.

For this attack of vertigo he was treated in the hospital at Pretoria. After a fortnight he was again able to speak in so far as to make himself intelligible, although he never completely recovered his voice; swallowing too was performed normally again at this time.

After two months he began to walk about again with the aid of a stick. Since the attack however his sense of taste had suffered much After three months the double vision had disappeared too.

He did not suffer from *headache* either before or during the attack of vertigo. Neither had there been *any vomiting*, nor *singultus*.

It left however some lasting symptoms, to wit:

1. formications (needle-prickings), in the right half of the body and in the left half of the face.

2, his right eye seemed to him to be covered by a film.

3. he (is) was unable to distinguish between cold and heat with his right hand.

<sup>1</sup>) Later, more accurate measurements, which however have not yet been completely finished, seem to show that in this region a small deviation from the  $T^3$ -law exists which slightly surpasses the amount mentioned above. [Added in the translation].