

MEASUREMENTS OF THE SPECIFIC HEAT OF THALLIUM AT LIQUID HELIUM TEMPERATURES

by W. H. KEESOM and J. A. KÖK

(Communication No. 230c from the Kamerlingh Onnes Laboratory at Leiden)

Summary

Specific heats of thallium were measured from 1.3 to 4.2° K. The atomic heat of thallium shows a change of 0.00148 cal/°K. mol. at the transition point. This agrees with Rutgers' equation. No latent heat was observed at the transition point.

§ 1. *Introduction.* These measurements are a continuation of the investigations made in this laboratory on the specific heats of superconductors ¹⁾.

The fact that for tin it was found that the specific heat makes a jump ²⁾ at the transition point from the superconductive to the non-superconductive state made it particularly desirable to extend our research to another superconductor. As such thallium presented itself because, if the abrupt decrease of the specific heat at the transition point should prove to be of the same order of magnitude as in the case of tin, it could be measured with sufficient accuracy.

We also made a number of experiments with a magnetic field being applied and with persistent currents going on in the metal. As, however, the discussion of the results of these experiments is not yet finished we limit ourselves in this paper to the description of the experiments with no magnetic field and no persistent currents.

1) H. Kamerlingh Onnes and G. Holst. Comm. No. 142c. Proc. Kon. Akad. Amsterdam 17, 762, 1914. W. H. Keesom and Donald H. Andrews. Comm. No. 185a. Proc. Kon. Akad. Amsterdam 30, 434, 1927. W. H. Keesom and J. N. van den Ende. Comm. No. 203d. Proc. Kon. Akad. Amsterdam 33, 243, 1930. Comm. No. 213c. Proc. Kon. Akad. Amsterdam 34, 210, 1931. Comm. No. 219b. Proc. Kon. Akad. Amsterdam 35, 143, 1932.

2) W. H. Keesom and J. N. van den Ende. Comm. No. 219b. W. H. Keesom and J. A. Kōk. Comm. No. 221e. Proc. Kon. Akad. Amsterdam 35, 743, 1932.

§ 2. *a. Apparatus.* For the method we refer to Comm. Nos. 203*d*, 219*b* and 221*e*.

We used the same measuring and heating core as was mentioned in Comm. No. 219*b*.

In Comm. No. 219*b* §4*a* attention was drawn to the fact that at about 1.48° K. the heat capacity of the core made a jump, caused by the liquefaction of part of the helium enclosed. So we reduced the helium pressure in the core to 5 cm at 20° C., to the effect that condensation would occur at 1.05° K. In connection with this a correction was applied to the heat capacities of the core.

Moreover because of a damage of the glass parts of the core the phosphorbronze wire had to be slightly shortened and another constantan thermometer wire was taken. They were calibrated in the ranges of liquid helium and hydrogen, the temperatures being calculated from the vapour pressures ¹⁾).

Using a Z e r n i k e galvanometer, with a measuring current of 0.4 mA, 10 cm on the scale corresponded to a temperature change of 0.01° K.

We made a dT/dR graph for calculating the temperature increase from the change of the resistance of the thermometer wire.

b. A cylindrical block was cast from a number of bars of thallium K a h l b a u m in vacuo in a glass vessel ²⁾). The weight of the block was 731.1 g.

The heat capacities being throughout larger than in the measurements on tin and the vacuum being very good, we could determine the ideal temperature increases by extrapolating the fore- and after-periods of the temperature curve to the middle of the heating period³⁾).

§ 3. *Results.* We obtained the results recorded in table I. Those in liquid helium are represented in Fig. 1.

1) W. H. K e e s o m. Comm. Suppl. No. 71*d*. Rapp. et Comm. No. 4, 6e Congr. Int. du Froid, 1932. For liquid hydrogen temperatures: J. P a l a c i o s and H. K a m e r l i n g h O n n e s. Comm. No. 156*b*. Arch. Néerl. (IIIA) 6, 31, 1923.

2) S c h e r i n g-K a h l b a u m A.G. were so kind as to send us a qualitative chemical analysis. 5 g of thallium in nitric acid gave a colorless solution. The metal contains an evident trace of silver and is almost perfectly free from lead. Further it contains no copper, no tin, and no sesquioxides of thallium. Moreover, the transition point (2.36° K) coincides with that found by H. K a m e r l i n g h O n n e s and W. T u y n, Comm. No. 160*a*, Proc. Kon. Akad. Amsterdam 25, 443, 1922, and by W. J. d e H a a s and J. V o o g d, Comm. No. 212*d*, Proc. Kon. Akad. Amsterdam 34, 51, 1931.

3) Cf. W. H. K e e s o m and J. A. K o k. Comm. No. 219*c*. Proc. Kon. Akad. Amsterdam 35, 294, 1932.

TABLE I

Atomic heat of thallium							
No.	Heat supplied cal.	Temperature °K	Temperature increase °K	Total heat capacity cal/°K	Heat capacity core cal/°K	Atomic heat thallium cal/°K mol	θ °K
November 18th, 1932 (in liquid helium)							
Ia	0.0003620	1.297	0.04469	0.008100	0.000430	0.002172	77.1
b	0.0003754	2.012	0.01291	0.02907	0.00074	0.007921	78.1
c	0.0005497	2.058	0.01794	0.03064	0.00076	0.008354	78.5
d	0.0004693	2.073	0.01443	0.03252	0.00077	0.008877	77.5
e	0.0004157	2.140	0.01182	0.03517	0.00080	0.009610	77.7
f	0.0004023	2.169	0.01095	0.03674	0.00081	0.01005	77.7
g	0.0004023	2.188	0.01112	0.03618	0.00082	0.009886	79.1
h	0.0004023	2.204	0.01028	0.03913	0.00083	0.01071	77.4
i	0.0004023	2.270	0.009603	0.04189	0.00087	0.01147	78.0
j	0.0004023	2.291	0.008916	0.04512	0.00088	0.01237	76.7
k	0.0004023	2.328	0.008612	0.04671	0.00089	0.01281	77.1
l	0.0004023	2.353	0.008573	0.04693	0.00091	0.01287	77.7
m	0.007216	2.898	0.09943	0.07257	0.00124	0.01994	82.7
n	0.008355	3.145	0.09386	0.08901	0.00138	0.02450	83.8
IIa	0.02026	3.147	0.2279	0.08891	0.00139	0.02447	84.1
b	0.02092	3.348	0.1995	0.1048	0.0015	0.02888	84.5
c	0.02615	3.515	0.2152	0.1215	0.0016	0.03352	84.4
d	0.03334	3.701	0.2422	0.1376	0.0017	0.03800	85.2
e	0.05238	3.943	0.3247	0.1613	0.0019	0.04457	86.1
f	0.08935	4.183	0.4592	0.1946	0.0022	0.05379	85.9
November 25th, 1932 (in liquid helium)							
Ia	0.0004467	1.590	0.03236	0.01380	0.00055	0.003706	79.5
b	0.0007055	1.957	0.02641	0.02671	0.00074	0.007261	78.2
c	0.0007055	2.098	0.02157	0.03270	0.00078	0.008925	78.3
d	0.0007055	2.190	0.01866	0.03781	0.00082	0.01034	77.9
e	0.0006820	2.208	0.01692	0.04031	0.00083	0.01104	76.7
f	0.0007055	2.230	0.01795	0.03930	0.00084	0.01075	78.3
g	0.0007055	2.247	0.01671	0.04222	0.00085	0.01157	77.0
h	0.0007525	2.272	0.01755	0.04288	0.00087	0.01175	77.4
i	0.0007055	2.288	0.01634	0.04317	0.00088	0.01182	77.8
j	0.0007055	2.304	0.01554	0.04540	0.00088	0.01245	77.0
k	0.0007055	2.320	0.01600	0.04409	0.00089	0.01208	78.4
l	0.0007074	2.335	0.01526	0.04636	0.00090	0.01271	77.5
m	0.0007074	2.350	0.01460	0.04845	0.00091	0.01329	79.1
n	0.0007074	2.368	0.01600	0.04421	0.00091	0.01211	79.9
o	0.0007074	2.384	0.01643	0.04306	0.00092	0.01178	81.2
p	0.0007074	2.401	0.01549	0.04567	0.00094	0.01251	80.1
q	0.0007074	2.420	0.01606	0.04405	0.00095	0.01205	81.8
r	0.0007074	2.439	0.01527	0.04633	0.00096	0.01268	81.0
s	0.0007074	2.456	0.01460	0.04845	0.00097	0.01327	80.3
t	0.0007074	2.479	0.01456	0.04859	0.00098	0.01331	81.0
u	0.0007074	2.500	0.01386	0.05104	0.00099	0.01399	80.3
v	0.0007074	2.519	0.01361	0.05198	0.00100	0.01425	80.4
December 21st, 1932 (in liquid helium)							
IIIa	0.0004050	1.310	0.05042	0.008033	0.00044	0.002122	78.8
b	0.0004185	1.338	0.04880	0.008577	0.00045	0.002272	78.8
December 1st, 1932 (in liquid hydrogen)							
Ia	4.689	16.517	0.666	7.037	0.090	1.940 ¹⁾	88.9
b	5.791	17.961	0.779	7.441	0.119	2.044	93.8
c	7.549	18.819	0.892	8.462	0.139	2.324	90.8

1) A correction from c_p to c_v , amounting to 0.003 at 18.8° K, was applied.

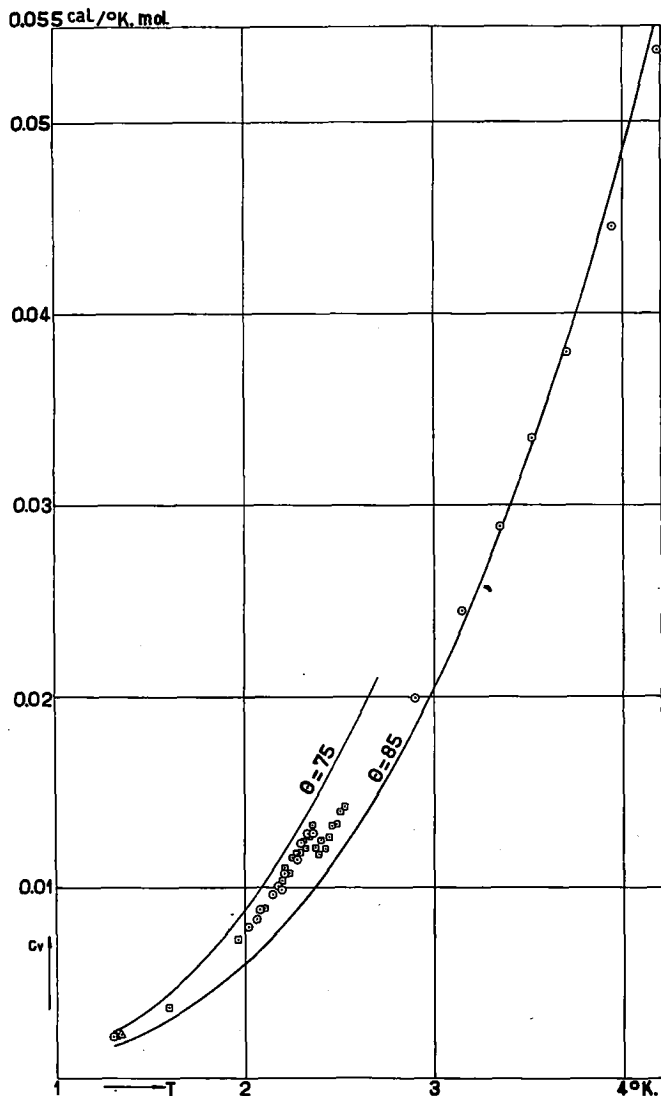


Fig. 1. Atomic heats of thallium.

○ Nov. 18th, 1932. □ Nov. 25th, 1932. △ Dec. 21st, 1932.

No latent heat was observed in passing the transition point.

We also made some few measurements at liquid hydrogen temperatures. They have been inserted in Table I. They agree quite well with the measurements of Clusius and Vaughan¹⁾.

1) K. Clusius and J. V. Vaughan. Journ. Am. Chem. Soc. 52, 4686, 1930.
Previous measurements: W. Nernst und F. Schwers, Berlin Sitzber. 1914, 355.

We deduced a smoothed curve of the values of θ and calculated from them atomic heats for regular temperatures (Table II, fig. 2).

TABLE II.

Atomic heat of thallium. Smoothed values					
T °K	θ °K	c_v cal/°K mol	T °K	θ °K	c_v cal/°K mol
1.3	78.82	0.002084	2.36	77.23	0.01325
1.4	78.75	0.002610	2.36	80.36	0.01177
1.5	78.66	0.003221	2.4	80.55	0.01229
1.6	78.60	0.003918	2.5	81.01	0.01365
1.7	78.48	0.004722	2.6	81.46	0.01510
1.8	78.36	0.005630	2.7	81.92	0.01663
1.9	78.23	0.006654	2.75	82.18	0.01741
2.0	78.10	0.007800	3.0	83.28	0.02171
2.1	77.89	0.009103	3.5	84.90	0.03254
2.2	77.69	0.01055	4.0	85.83	0.04702
2.3	77.40	0.01219	4.2	86.13	0.06625

At 2.36 °K: $\Delta c = 0.00148$ cal/°K mol.

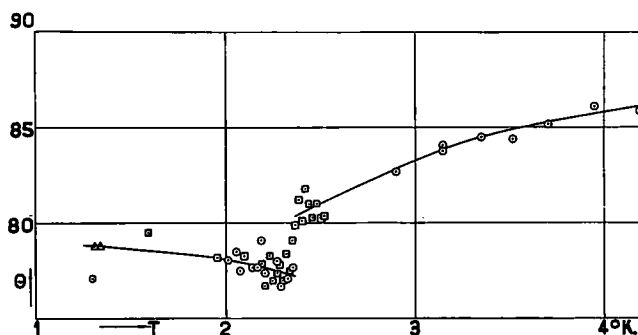


Fig. 2. Debije characteristic temperatures for thallium.
 ○ Nov. 18th, 1932. □ Nov. 25th, 1932. △ Dec. 21st, 1932.

§ 4. *Discussion.* *a.* It appears from the results given in § 3 that the atomic heat of thallium at 2.36° K. falls from 0.01325 to 0.01177.

In comparing with the similar result for tin, we observe that there is no simple connection between the jump in the atomic heat Δc and the Debije characteristic temperature θ .

For these two substances the relation $\Delta c/T = \text{const.}$ rather nearly holds ($T = \text{transition point}$).

Rutgers¹⁾ deduced the equation

$$\left(\frac{dH}{dT}\right)^2 = \frac{4\pi \Delta c}{TV}.$$

1) A. J. Rutgers, see P. Ehrenfest, Suppl. No. 75b. Nachtrag bei der

V = atomic volume at the transition point. dH/dT = the derivative of the threshold value of the magnetic field at the normal transition point. We collected in Table III the data now available to check that equation.

TABLE III

Verification of Rutgers' equation.					
	T °K	V cm ³ /mol.	dH/dT gauss/°K	Δc calc. cal/°K mol	Δc obs. cal/°K mol.
tin	3,71	8,37	151,2	0,00229	0,0024
thallium	2,36	16,9	137,4	0,00144	0,00148

It may be noted that the agreement between observed and calculated values of Δc is very satisfactory.

b. Considering the variations of θ for thallium with temperature the following points suggest themselves:

- α . The variations of θ with temperature are very moderate throughout, just as is the case with Pb and Bi which have values of θ of about the same magnitude.
- β . Somewhere above 4.2° K. a steeper decrease of θ with decreasing temperature (to 2.4° K.) seems to set in. This decrease is, however, considerably less steep than for Ag and Zn .
- γ . The impression, that the θ , T -curves of the different metals seem to converge to about the same point at 0° K., as expressed previously by one of us ¹⁾, is rather corroborated by the behaviour of thallium.
- δ . It looks as if the θ , T -curve for the supraconductive condition converges to about the same point at 0° K., as the extrapolatory production of the θ , T -curve for the non-supraconductive condition.

Of course it is to be understood that in these statements, for so far as Debye's law is no more valid, θ has no other meaning ²⁾ than that of a quantity proportional to $c_v^{-1/3}$. So the statement under γ , if confirmed by further measurements, would only mean that the

Korrektur. Proc. Kon. Akad. Amsterdam 36, 153, 1933. Cf. C. J. Gorter, Arch. d. Musée Teyler III, 7, 378.

1) W. H. Keesom. Rapp. et Comm. 6ième Congr. Int. du Froid 1932, No. 9, § 2a.

2) Cf. W. H. Keesom and H. Kamerlingh Onnes, Comm. No. 143, p. 24, note 3. Proc. Kon. Akad. Amsterdam, 17, 912, 1914. Comm. No. 147a § 4. Proc. Kon. Akad. Amsterdam 18, 491, 1915.

atomic heat of metals at temperatures about 1° K., approaches to a value which is independent of the nature of the individual metal, hence, for the greater part at least, is not determined by atomic weight and interatomic forces as it is at higher temperatures.

We gladly express our thanks to phil. nat. cand. A. P. K e e s o m for her valuable assistance during the measurements, and to Mr. C. W. C l a r k M. Sc. for the many calculations he has made for us.