

*Citation:*

H. Kamerlingh Onnes & W.H. Keesom, The specific heat at low temperatures. III. Measurements of the specific heat of solid nitrogen between 14°K. and the triple point and of liquid nitrogen between the triple point and the boiling point, in:

KNAW, Proceedings, 18 II, 1916, Amsterdam, 1916, pp. 1247-1255

validity of that term has been proved with still greater certainty as to its *absolute* value. Especially the measurements in the blue part of the spectrum have here the greatest convincing power.

Finally I wish to express my thanks to Miss C. M. PEERBOOM assistant at the Physical Laboratory, Amsterdam, for her assistance in part of the experiments and of the calculations and to Mr. J. VAN DER ZWAAL, mechanic of the Laboratory for his assistance in making the apparatus.

10. In one respect the experiments can teach still something on the question whether the length of the moving water-column with which the calculations have been carried out, has been fairly well chosen.

According to these Proceedings (Vol. 18, 401, 1915) I took for this length the distance between corresponding points of intersection of the axes of the *O*-shaped supplying-tubes with the axis of the apparatus. With the apparatus described in § 2 I have been able to prove that this was the right length. Through the window *V* stream-lines can be observed, if a vertical plane through the axis of the tube is illuminated. With an accuracy of some millimeters we can indicate in which point the stream-lines become rather suddenly parallel to the axis of the tube *ED*, while on the left of that point the fluid is nearly at rest. There cannot exist any doubt whether the motion must be reckoned from the point *V* indicated in the Figure. On the whole length of FIZEAU's tube i.e. 302 cm. the inaccuracy of some millimeters in the determination of the place of *V* is of no consequence.

**Physics.** — “*The specific heat at low temperatures. III. Measurements of the specific heat of solid nitrogen between 14° K. and the triple point and of liquid nitrogen between the triple point and the boiling point.*” By W. H. KEESOM and H. KAMERLINGH ONNES. Communication N°. 149a from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 29, 1916).

§ 1. The investigation of the specific heat of condensed monatomic and di-atomic gases appears of special interest with a view to the conclusions, which may be drawn about the crystal structure from the comparison of the specific heat in the solid state for these two groups of substances. In particular the question arises whether for the last mentioned group of substances their di-atomic nature does or does not show itself in the solid state also.

§ 2. We began with the investigation of the specific heat of

nitrogen <sup>1)</sup>. We measured the specific heat of solid and of liquid nitrogen with the aid of the apparatus represented in Figs. 1 and 2.

The gas, which was first passed from the cylinder *B* (Fig. 1)

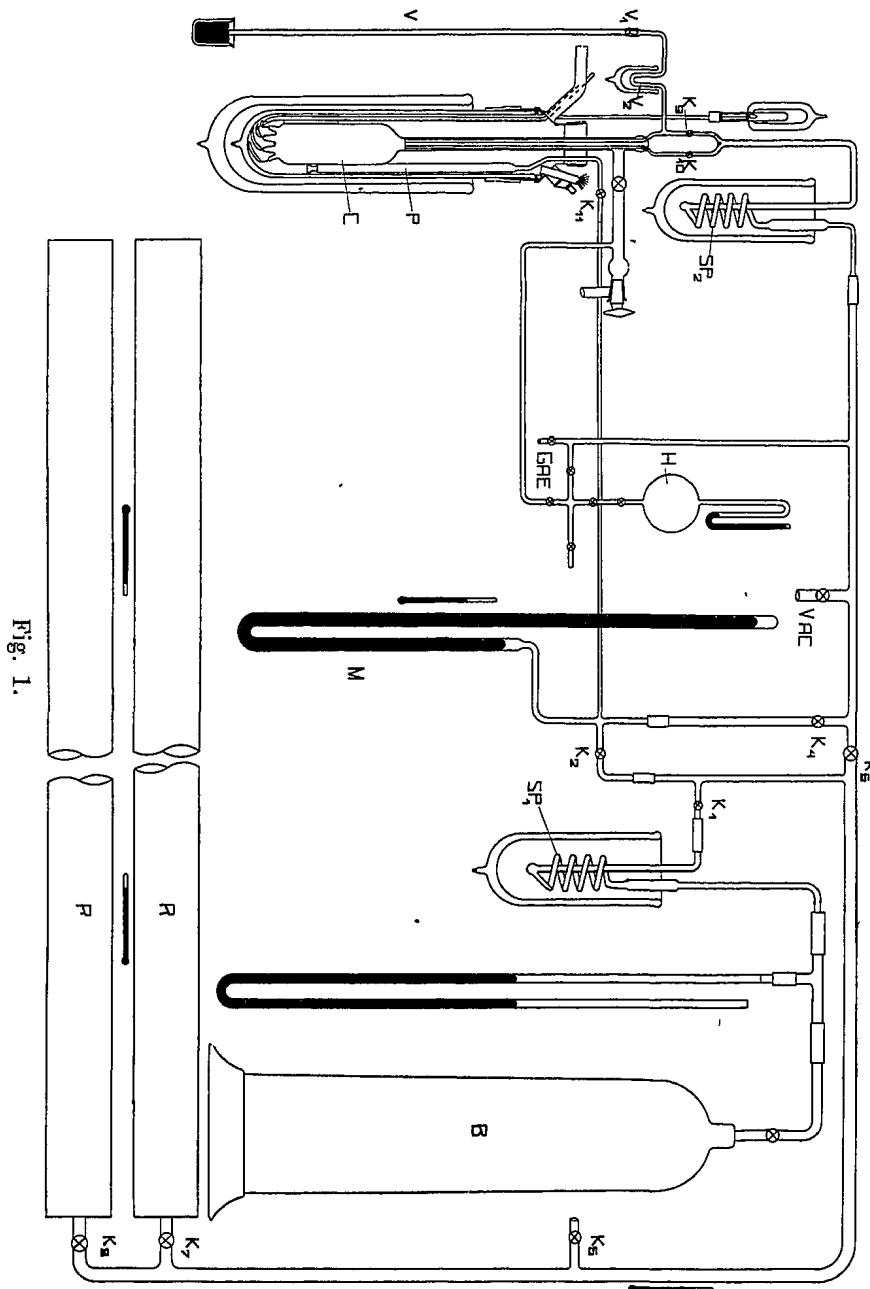


Fig. 1.

<sup>1)</sup> While this communication was being printed we received the number of January 15th of the Verh. d. D. physik. Ges., in which EUCKEN publishes the results of his measurements on specific heats etc. of compressed and condensed gases, amongst which is also nitrogen. Our results agree in general with those of EUCKEN concerning nitrogen.

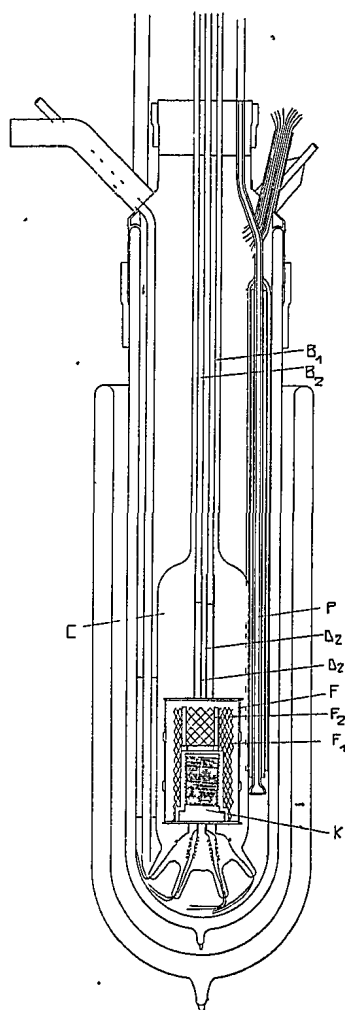


Fig. 2.

The spiral  $Sp_2$ , which was cooled in liquid air, serves for retaining the last traces of moisture and other vapours. To prevent a deposition of solid nitrogen in the glass inlet tube  $b_1$  (continued by the copper tube  $d_1$ , internal diameter 3 mm.), and to get the calorimeter properly filled, the cooling was performed very slowly from below upwards. The condensation process was checked with the manometer  $M$  and for the measurements on solid nitrogen was continued until at the triple point the nitrogen, as calculated from the volume of the calorimeter and the density of the liquid, filled the flask  $F$  to a little below the top. For safety a second tube  $b_2, d_2$  was provided, by which the gas, if  $b_1$  or  $d_1$  should become obstructed, can escape through the safety tube  $v$  (provided with a strike-back safety-valve  $v_1$  for the mercury and a  $U$ -tube  $v_2$  cooled in liquid air for protecting the calorimeter from mercury vapour), or else be led back to  $R$  through  $k_1$ .

Through the bottom a chamber is let in into  $F$ , into which the

through the drying spiral  $Sp_1$ , cooled in liquid air to the reservoirs  $R$ , was condensed in the calorimeter flask  $F$  (Fig. 2). The heat capacity of this flask (provided with heating and thermometer wires) with the condensed gas in it was then measured by the method of electrical heating in a high vacuum (cf. Comm. N<sup>o</sup>. 143, these Proc. December '30, 1914).

The capacity of the steel reservoirs  $R$  (together about 45 L., the same reservoirs which served for the measurement of the heat of vaporization of hydrogen, Comm. N<sup>o</sup>. 137e), and of the connections as far as necessary, was accurately determined by the volumetric method, using two glass bulbs (together 4.5 L.) calibrated with water. The quantity of gas, which was condensed in  $F$ , was calculated from the pressures of the gas in  $R$  before and after, taking into account the gas which remained in the connections. For a check after the measurements the gas was collected from the calorimeter into  $R$  and measured again.

core  $K_{III}$  with heating and thermometer wires (Comm. N<sup>o</sup>. 143, Oct. 1914, N<sup>o</sup>. 147a, June 1915) is screwed.

For the purpose of promoting the heat conduction in the condensed gas a quantity of copper gauze  $f_1$  is introduced into the flask and soldered to the walls. Three copper rods  $f_2$  serve the same purpose, particularly also to prevent that, when the solidified gas melts again and vaporizes, that part of it which is nearest to the openings of the tubes  $d_1, d_2$ , should remain solid longer than the other part and so obstruct the streaming off of the liquid or the gas. Moreover from the reservoir  $H$  a small quantity of hydrogen gas could be introduced to convey the heat between the crystals or parts of the solid gas which might lie side by side thermally isolated, when the vapour pressure of the condensed gas is too small to provide itself for the heat convection.

The conduction of heat in the nitrogen appeared to be sufficiently rapid, to render the temperature uniform within a couple of minutes after the heating in the calorimetric experiment. On the other hand the heat conduction through the glass tubes  $b_1, b_2$  was sufficiently small, so that with a good vacuum inside the calorimeter glass the temperature of the calorimeter showed before and after the experiment a sufficiently slow rate of change. As examples we give in Figs. 3a and b the galvanometer-curve in two measurements (at 15.3 and 61.7° K. respectively, cf. table I).

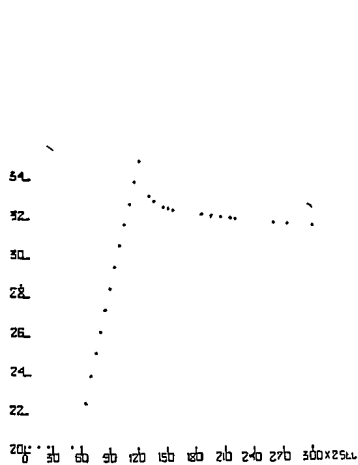


Fig. 3a.

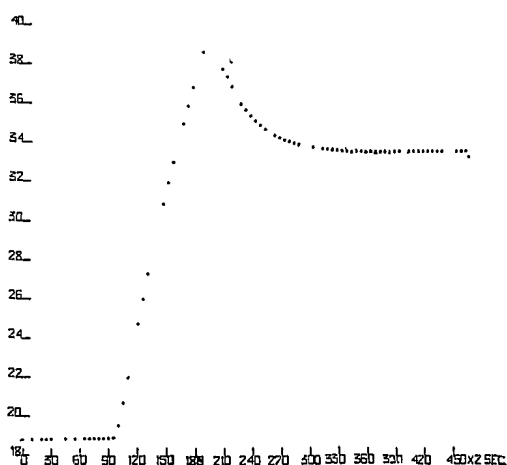


Fig. 3b.

The capacity of the flask  $F$  is about 50 ccm.

For the measurements we refer further to the description in Comm. N<sup>o</sup>. 143 § 2, for the charcoal tube for keeping up the vacuum, which is left out in Fig. 1, to Comm. N<sup>o</sup>. 143 Fig. 1.

As explained in Comm. N<sup>o</sup>. 147a (These Proceedings September 1915, p. 485 note 3) the scale of the thermometer wire  $Au_{c3}$  in the

region of liquid hydrogen temperatures was each time determined at least at two temperatures, viz. at about 20,3 and 14° K. For this purpose the vapour pressure of the hydrogen in the cryostat bath was measured with the aid of a vapour pressure tube  $p$ . The vapour pressure was read (the stop-cock  $k_{11}$  being opened) on the manometer  $M$ .

For the measurement of the temperatures<sup>1)</sup> we refer to Comm. N°. 143 § 2 and 147a § 1.

The heat capacity of the calorimeter flask  $F$  (of copper) with the core  $K_{III}$  was determined by special measurements in liquid hydrogen and in liquid air.

### § 3. *The triple point of nitrogen.*

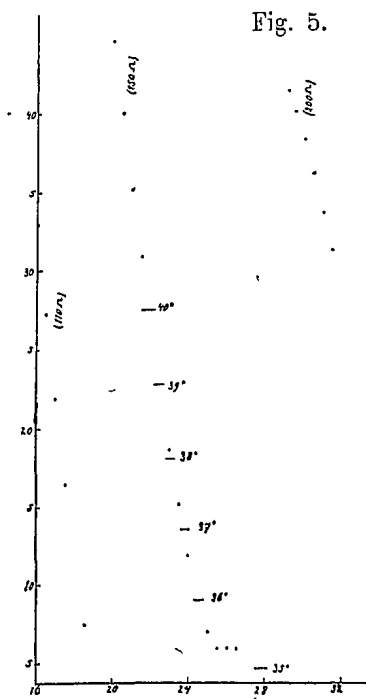
The nitrogen was prepared and treated in the same way as the gas which served for the measurements of Comm. N°. 145b, c and d (cf. Comm. N°. 145b § 2), so that we may rely on a high degree of purity. In fact the analysis with copper in ammonia (HEMPPEL) as well as that with pyrogallic potash yielded less than 0.1% for the admixture of oxygen.

For the temperature of the triple point of nitrogen we found 63.06° K. This temperature lies higher than that found by FISCHER and ALT<sup>2)</sup>: — 210.50° on a hydrogen-thermometer with  $p_0 = 96$  cm., lower than that derived by HOLST<sup>3)</sup> from the measurements of v. SIEMENS.<sup>4)</sup>

1) We gladly record our cordial thanks to Messrs. P. G. CATH and J. M. BURGERS for their aid in these measurements.

2) K. T. FISCHER und H. ALT. Ann. d. Phys. (4) 9 (1902), p. 1149.

3) G. HOLST. Comm. N°. 148a (Sept. '15).



4) In order to see whether transformation points occur in solid nitrogen, on cooling below the triple point the time-rate of the temperature was followed continuously. Originally on examining our cooling curves the presence of a transformation point had escaped us through a combination of fortuitous circumstances. On a renewed examination, made in consequence of the fact that EUCKEN (p. 1248 note 1) found a transformation point, it appears that our observations confirm its existence.

In fig. 5 (ordinates: galvanometer readings, abscissae: minutes) we give a part of one of the cooling curves. Three different cooling curves point to a transformation at 35.3, 35.4, 35.3° K., whereas in a temperature curve taken during heating an indication of the beginning of a transformation occurs at 36.4° K. Down to 14.55° K. we did not find any indication of the existence of a further transformation point.

## § 4. Atomic heat of solid nitrogen.

In table I the results of the measurements concerning solid nitrogen have been collected.

TABLE I.

Atomic heat of solid nitrogen.						
No.	Quantity of nitrogen in grs.	Mean temp.	Temperature increase	Heat capacity of nitrogen + flask and core <i>KIII</i> in joules/degree K.	Heat capac. of flask and core <i>KIII</i> in joules/degree K.	Atomic heat of nitrogen in cal <sub>15</sub> /degree K. <i>C<sub>p</sub></i>
13 July I	40.3	15.27	1.438	20.63	1.32	1.60
13 " II	"	16.50	1.306	22.60	1.57	1.74 <sup>5</sup>
13 " III	"	20.75	0.904	32.69	2.64	2.49
12 " I	42.1	20.78	0.875	33.29	2.65	2.43 (weight 1/2)
12 " II	"	20.93	0.852	34.31	2.70	2.51
22 June I	40.4	21.71	0.662	32.82	2.95	2.47
12 July III	42.1	39.16	0.316	67.6	12.1	4.41
12 " IV	"	39.40	0.310	68.8	12.2	4.50
22 June II	40.4	45.88	0.696	73.7	16.5	4.74
23 Oct. I	40.5	55.26	0.722	86.1	23.6	5.16
23 " II	"	56.04	0.731 <sup>5</sup>	86.5	24.1 <sup>5</sup>	5.15
27 Nov. II	42.6	56.12	0.702 <sup>5</sup>	88.4	24.1	5.05
27 " III	"	56.85	0.691	90.9	24.7	5.19 <sup>5</sup>
27 " IV	43.7 <sup>5</sup>	61.32	0.631	96.7	27.7 <sup>5</sup>	5.27
23 Oct. III	40.5	61.68	0.668	94.3	28.0	5.48

The results for  $C_p$  are represented in fig. 4, together with those of § 5 concerning liquid nitrogen.<sup>1)</sup> (See fig. 4 following page).

In this figure have also been drawn the curves, which are obtained from DEBIJE's formula for  $C_v$  with  $\theta = 90$  and with  $\theta = 100$ , with which the course of the atomic heat of solid nitrogen agrees in its main features.<sup>2)</sup>

A closer comparison with the theoretical formulae which have

<sup>1)</sup> Our results are between 39 and 62° K. about 2% smaller than those of EUCKEN.

<sup>2)</sup> Apparently the transformation of nitrogen (p. 1251 note 4) has not a great influence on the value of  $\theta$ .

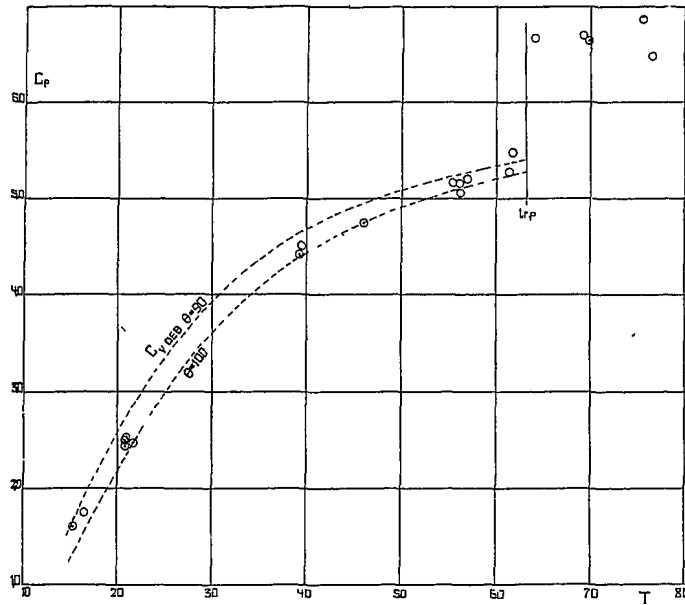


Fig. 4.

been derived for  $C_v$ , is made difficult by the fact that the difference  $C_p - C_v$  is not known for solid nitrogen.

If this difference is taken from the relation given by NERNST and LINDEMANN <sup>1)</sup>:

$$C_p - C_v = A_0 \frac{T}{T_s} C_p^2,$$

and if for  $A_0$  the value 0,021 is chosen as found for monatomic metals and for salts which behave as if they were monatomic, the following values for  $C_p - C_v$  are found:

$T = 15,3$	$21$	$40$	$62$
$C_p - C_v = 0,01$	$0,04$	$0,29$	$0,50$

If these values for  $C_p - C_v$  are taken it appears that <sup>2)</sup>  $C_v$  deviates from DEBIJE'S formula in the same sense as sulphur and graphite. This would lead to the conclusion that the specific heat of nitrogen in the solid state does not change like that of the monatomic solid substances mentioned above. But then the basis for the calculation of  $C_p - C_v$  <sup>3)</sup> breaks down.

<sup>1)</sup> W. NERNST and F. A. LINDEMANN, ZS f. Elektrochem. 17 (1911), p. 817.

<sup>2)</sup> For both parts of the curve, which relate to the two modifications (p. 1251 note 4).

<sup>3)</sup> That for solid elements which are not monatomic a different value of  $A_0$  may occur in the formula of NERNST and LINDEMANN, becomes apparent if  $C_p - C_v$  is calculated for sulphur and for phosphorus at 20° C. from the compressibility according to RICHARDS, J. Amer. Chem. Soc. 37 (1915), p. 1644, and from the coefficient of expansion (comp. also RICHARDS l.c.). From these data follows (for 20° C.): for sulphur (rhombic):  $A_0 = 0.012$ , for phosphorus (white):  $A_0 = 0.026$ .



Meanwhile it is sufficiently clear that nitrogen deviates from the behaviour of monatomic solid substances such as copper, lead etc. In particular the specific heats at the liquid hydrogen temperatures, at which  $C_p - C_v$  very probably has still small values, point in this direction. The same follows also when  $\theta$  is calculated from LINDEMANN'S formula (Comm. N<sup>o</sup>. 147a § 5):  $k_L = 2,81$ ,  $T_s = 63$ ,  $v_M = \frac{14,01}{1,026^5}$  according to DEWAR at  $-252,5^\circ$  C. give  $\theta = 120$ , i.e. a value which is considerably too high.

Hence presumably nitrogen is in the solid state also di-atomic<sup>1)</sup>, i.e. the crystal space lattice<sup>2)</sup> is composed of 2 point systems placed one inside the other in an analogous way as for instance the space lattice of rhombic sulphur is built up from 8 interpenetrating (rhombic) point systems, in such a way that a new frequency is introduced by the vibrations of the two point systems with respect to each other.

#### § 5. *Specific heat of liquid nitrogen.*

With the aid of the apparatus described in § 1 some measurements were also made of the specific heat of liquid nitrogen.

When the vapour pressure of the liquid attains an appreciable value, a correction has to be applied for the evaporation caused by the temperature increase in the calorimetric experiment. For this purpose the increase of pressure was read on the safety tube  $v$ . The quantity which has vaporized then follows from the approximately known volume between  $k_s$ ,  $k_{10}$ , the solid nitrogen in  $F$  and the mercury in the safety tube  $v$ . This correction was always small: at the highest temperature it amounted only to 0.8 % of the heat supplied.

In table II the data concerning liquid nitrogen are given<sup>3)</sup>.

<sup>1)</sup> This conclusion was already drawn by NERNST and LINDEMANN, Berlin Sitz. Ber. 1912, p. 1170 from the low triple point of nitrogen in connection with its possessing subsidiary valencies.

<sup>2)</sup> For both the modifications (p. 1251 note 4). As according to W. WAHL. Proc. Roy. Soc. A 87 (1912), p. 371, ZS physik. Chem 84 (1913), p. 101, nitrogen below the triple point at first crystallizes in the cubic system, those point systems must be cubic for the modification which is stable at the higher temperatures.

<sup>3)</sup> Strictly speaking the values given in table II for the specific heat and the atomic heat are valid for the liquid under the pressure of its saturated vapour; within the degree of accuracy of the measurements they may be considered to coincide with  $c_p$ , and  $C_p$  respectively.

TABLE II.

Specific heat of liquid nitrogen.							
No.	Quantity of nitrogen in grammes	Mean temperature	Temperature increase	Heat capacity of nitrogen + flask and core $K_{III}$ in joules/degree K.	Heat capacity of flask + core $K_{III}$ in joules/degree K.	Specific heat of nitrogen in cal <sub>15</sub> /degree K.	Atomic heat in cal <sub>15</sub> /degree K.
29 Nov.	-						
II	41.7	63.95	0.585	112.6	29.5	0.476	6.67
III	"	69.15	0.564	116.2	32.8	0.478	6.70
IV	"	69.73	0.566	115.9	33.2	0.474	6.64
VI	41.6	75.46 <sup>5</sup>	0.727	121.9	36.4	0.490	6.87
V	"	76.49	0.752	117.6	37.0	0.462 <sup>5</sup>	6.48

The values of the atomic heat of liquid nitrogen are also given in Fig. 4.

The sudden increase of the atomic heat at the triple point appears to amount to 1.3 cal.

The value found by us for the specific heat of liquid nitrogen is considerably higher than that given by ALT<sup>1)</sup>: 0.430 for the mean specific heat between 65° and 77° K.

**Zoology.** — “*On the phylogenetic significance of the Wing-markings in Hepialids*”. By J. F. VAN BEMMELLEN.

(Communicated in the meeting of January 29, 1916).

My previous investigations of the colour-markings on the wings of Lepidoptera have led me to certain conclusions, which may be briefly summarised here, as they are needed for the better understanding of the phenomena on the wings of the primitive Hepialid family.

The first conclusion is that the colour-pattern is to be looked upon as a mixture of components of different phylogenetic age, and consequently of unequal systematic value.

Of the facts on which this conclusion is based, three may be mentioned here:

1. During the development of the wings inside the pupal sheath

<sup>1)</sup> H. ALT, Ann. d. Phys. (4) 13 (1904), p. 1010.