Physics. — *Measurements about the Velocity of Sound in Nitrogen Gas.* By W. H. KEESOM and J. A. v. LAMMEREN. (Communication N⁰. 221*c* from the KAMERLINGH ONNES-Laboratory at Leiden).

(Communicated at the meeting of June 25, 1932).

§ 1. *Introduction.* In Comm. Nos. 209*a* and *c* and 213*b* [1]) W. H. KEESOM and A. v. ITTERBEEK reported on an apparatus suitable for the determination of the velocity of sound in gases at low temperatures. This apparatus we now used to make measurements in nitrogen gas at temperatures extending from 0° C. down to the liquid nitrogen range. As shown by the authors mentioned it is possible, by measuring the velocity of sound in dependence on the pressure, to calculate the ratio c_p/c_v and the second virial coefficient B as a function of the temperature.

In these experiments we considered more closely the influence of the resonator, this influence being of high importance when extrapolating the velocity of sound to a pressure $p=0$.

§ 2. *Experimental methods.* For the methods we refer to Comm. N⁰. 213*b*. The temperature was determined by means of two platinum resistance thermometers. We used four resonators indicated by R_I, R_{II}, R_{III} (brass tube) and R_{IV} (copper tube), the dimensions of which are given in table I.

TABLE I.

Resonator	Diameter mm	Length mm 0° C.
R_I brass	62	297.7
R_{II} „	36	804.8
R_{III} „	35	299 0
R_{IV} copper	35	801.4

R_{IV} was made of copper in order to obtain a more uniform temperature in the long cryostat needed.

In view of the influence of the end-openings in the resonator we have always given these openings exactly the same diameter (1 mm). The nitrogen was obtained by heating sodium azide NaN_3, spread out in a horizontal glass tube. The gas was liquefied in a condenser cooled with liquid air boiling under reduced pressure. After fractional evaporation it was led into the resonator. This method guarantees a sufficient degree of purity.

---

[1]) W. H. KEESOM and A. VAN ITTERBEEK. These Proceedings **33**, 440, 1930; **34**, **204**, 1931; Comm. Leiden Nos. 209*a* and 213*b*. A. VAN ITTERBEEK and W. H. KEESOM, Wis- en Natuurk. Tijdschrift **5**, 69, 1930; Comm. Leiden No. 209*c*.

§ 3. *Experimental results.* *a.* Measurements at 0° C., summarized in table II.

TABLE II.

Velocity of sound in nitrogen at 0° C.

Resonator	Pressure at	$W_{obs.}$ m/sec	W m/sec
R_I	0.9844	336.5_5	337.0_6
R_{II}	0.9937	336.3	337.1
R_{III}	0.9842	336.7	337.5

In this and following tables $W_{obs.}$ means the average value obtained from several observations and W the velocity of sound corrected for the influence of the wall. To calculate this correction we used the formula of KIRCHHOFF-HELMHOLTZ [1]).

From table II it appears that the influence of the end-openings of the resonator R_{III} is considerably greater than is the case for R_I and R_{II}, for which this influence is much diminished by the large diameter resp. length. Furtheron the correction in these resonators will prove to be very small.

The agreement between the results in R_I and R_{II}, when the formula of KIRCHHOFF-HELMHOLTZ is applied, is very satisfactory. Our value of the velocity of sound at 0° C. agrees rather well with that found by other observers [2]).

b. Measurements at temperatures of liquid ethylene. The results are communicated in table III.

TABLE III. Resonator R_I.

Velocity of sound in nitrogen at liquid ethylene temperatures.

T °K.	Pressure at	$W_{obs.}$ m/sec	W m/sec
166.03	1.0090	262.0	262.2
161.14	0.9925	257.9	258.1
156.53	0.9786	254.1	254.3
146.04	0.9506	245.8	246.0

---

[1]) Compare Comm. No. 209*a*.

[2]) G. SCHWEIKERT, Ann. d. Phys. (4) **48**, 593, 1915.
H. B. DIXON, C. CAMPBELL and A. PARKER, Proc. Roy. Soc. London (A) **100**, 1, 1921.

c. Temperatures of liquid oxygen and nitrogen, tables IV, V and VI.

TABLE IV. Resonator R_I.

Velocity of sound in nitrogen gas.			
T °K.	Pressure at	$W_{obs.}$ m/sec	W m/sec
90.37	0.9299	190.9_8	191.0_8
	0.7293	191.6_7	191.7_8
	0.5541	192.1_1	192.2_4
	0.4380	192.5_3	192.6_7
	0.3207	192.7_7	192.9_4
	0.1973	193.1_1	193.3_2
	0.1176	193.0_9	193.3_7
82.95	1.0146	181.7_9	181.8_7
	0.7957	182.7_2	182.8_1
	0.5953	183.3_2	183.4_2
	0.4179	183.9_7	184.0_9
	0.2923	184.4_8	184.6_3
	0.1921	184.8_2	185.0_8
	0.1022	185.2_8	185.5_3
77.95	0.9026	175.9_8	176.0_6
	0.7122	176.8_8	176.9_6
	0.5789	177.4_9	177.5_8
	0.4380	177.9_4	178.0_5
	0.3029	178.6_5	178.7_8
	0.2025	179.0_8	179.2_4
	0.1183	179.5_5	179.7_6
71.92	0.3879	170.8_1	170.9_1
	0.3382	171.0_2	171.1_3
	0.2627	171.5_1	171.6_3
	0.1931	171.9_2	172.0_6
	0.1188	172.4_4	172.6_3

TABLE V. Resonator R_{III}.

T °K.	Pressure at	$W_{obs.}$ m/sec	W m/sec
79.17	0.9633	177.2_8	177.4_0
	0.6410	178.7_1	178.8_7
	0.4515	179.4_2	179.6_1
	0.2921	180.0_6	180.3_0
	0.1560	180.8_9	181.2_2

TABLE VI. Resonator R_{IV}.

T °K.	Pressure at	$W_{obs.}$ m/sec	W m/sec
78.36	0.9088	176.4_4	176.5_8
	0.7083	177.3_4	177.5_0
	0.5270	178.0_8	178.2_6
	0.3692	178.7_0	178.9_2

The results of the tables IV, V and VI are compared in § 4*c*.

§ 4. *Calculations* 1).

a. 0° C and temperatures of liquid ethylene.

With the formulas deduced in Comm. N⁰. 209*c* 2) we calculated c_p/c_v, $(c_p/c_v)_{p=0}$, c_v and c_p from W (tables II and III). For that purpose through three values of B, derived by NIJHOFF 3) from the measurements of KAMERLINGH ONNES and VAN URK 4) in the corresponding temperature range, we laid a curve of the second degree in $1/T$, with which we could calculate the values of B, dB/dT and d^2B/dT^2.

The results of these calculations are given in tables VII and VIII.

TABLE VII. Resonator R_I, 0° C.

Presssure at	c_p cal/mole	c_v cal/mole	c_p/c_v	$(c_p/c_v)_{p=0}$
0.9844	6.97	4.97	1.402	1.400

From the value of $(c_p/c_v)_{p=0}$ it appears that the influence of the end-openings in Resonator R_I may be supposed to be negligible. Our value 1.402 for c_p/c_v agrees with 1.4018 found by BRINKWORTH 5) at 17° C.

---

1) Mol. weight M = 28.016.

2) loc. cit.

3) G. P. NIJHOFF, Diss. Leiden 1928. Comm. Leiden Suppl. No. 64*f*.

4) H. KAMERLINGH ONNES and A. TH. VAN URK. Comm. Leiden No. 169*d*.

5) J. H. BRINKWORTH, Proc. Roy. Soc. London (A) **111**, 124, 1926.

TABLE VIII. Resonator R_I.

Temperatures of liquid ethylene.					
T °K.	Pressure at	c_p cal/mole	c_v cal/mole	c_p/c_v	$(c_p/c_v)_{p=0}$
166.03	1.0090	7.00	4.97	1.407	1.400
161.14	0.9925	7.01	4.98	1.407	1.400
156.53	0.9786	7.03	5.00	1.406	1.398
146.04	0.9506	6.97	4.93	1.413	1.403

The small deviations of $(c_p/c_v)_{p=0}$ from the value 1.400 may be due to the fact that the temperature has not been very constant during the measurements.

b. Temperatures of liquid oxygen and nitrogen.

1. *Resonator* R_I. In Fig. 1 we plotted W as a function of the pressure.

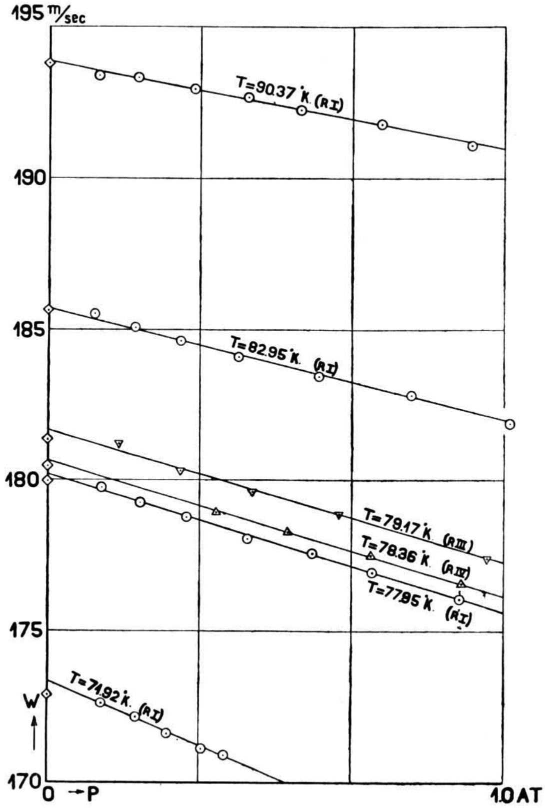

Fig. 1

It follows from Comm. N^0. 209*c* § 2 that it is possible to calculate a formula representing the change of the second virial coefficient B with T from the dependence of $\left(\frac{\partial W^2}{\partial p}\right)_{p=0}$ on the temperature.

We have tried to determine this function by representing the dependence of W^2 on the pressure by a quadratic formula in p with three coefficients. These coefficients were calculated by the method of least squares. We observe, however, that it is not possible to obtain certainty about the coefficient of p^2, on account of the comparatively small range of pressures. We therefore then determined only two coefficients by representing the dependence of W on the pressure by a linear formula. Thus we still obtain a quadratic dependence of W^2 on p.

So we postulated finally:

$$W = W_0 (1 + sp).$$

The coefficients W_0 and s were calculated from the data in table IV by means of the method of least squares.

From the coefficient W_0 the value $(c_p/c_v)_{p=0}$ can be derived by the relation:

$$\left(\frac{c_p}{c_v}\right)_{p=0} = \frac{M W_0^2}{RT} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

S is calculated from:

$$S = \frac{RT}{2 W_0^2} \left(\frac{\partial W^2}{\partial p}\right)_{p=0} = RT \, . \, s = B + \frac{T}{\lambda} \cdot \frac{dB}{dT} + \frac{T^2}{2 \lambda (\lambda + 1)} \cdot \frac{d^2 B}{dT^2}, \quad . \; . \quad (2)$$

where $\lambda = \frac{(c_v)_{p=0}}{R}$.

The results of these calculations are shown in table IX and plotted in Fig. 2 (indicated by ⊙).

TABLE IX.

T °K.	W_0 m/sec	s at^{-1}	$S \, . \, 10^3$	$(c_p/c_v)_{p=0}$
90.37	193.8_4	-0.01486	-4.919	1.400_7
82.95	185.7_0	-0.01979	-6.013	1.400_5
77.95	180.2_0	-0.02554	-7.291	1.403_4
71.92	173.3_4	-0.03705	-9.757	1.407_5

2. *Resonators R_{III} and R_{IV}.*

In view of the correction on the velocity of sound due to the resonator, we have controlled the measurements, mentioned in 1, using the resonators R_{III} and R_{IV} (table V and VI, indicated in Fig. 1 by ▽ resp. △). To be able to compare the results with those found in R_I we have also extrapolated to a pressure zero, but now with a coefficient s derived from the first measurements. See § 5.

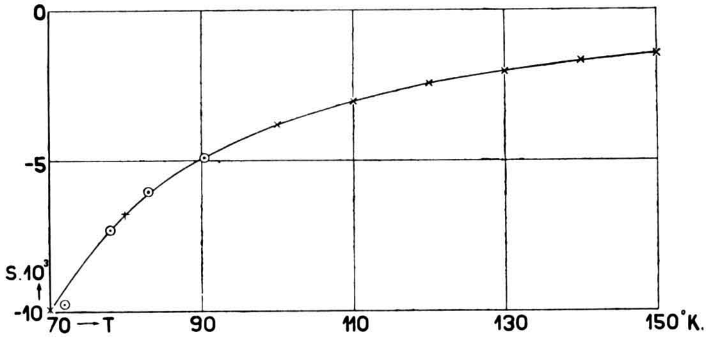

Fig. 2

The coefficient W_0 has been calculated by the method of least squares.

TABLE X.

Resonator	T °K.	s at^{-1}	W_0 m/sec	$(c_p/c_v)_{p=0}$
R_{III}	79.17	−0.02505	181.67	1.404_4
R_{IV}	78.36	−0.02409	180.66	1.403_2

At these temperatures the influence of the end-openings proves to be perceptible in resonator R_{III}, although this influence is much smaller than at 0° C.

Here also we obtain a good agreement by applying the formula of KIRCHHOFF-HELMHOLTZ.

3. We observe (tables IX and X), that $(c_p/c\ )_{p=0}$ slightly exceeds the value 1.400, the more so as the temperature is lower. If, however, we calculate ¹) theoretically the part of c_v corresponding to the rotational movement of the molecules, deriving the moment of inertia of the nitrogen molecule from RASETTI ²), we find that the rotational energy must have already reached the classical value.

At 90.37 and 82.95° K. the agreement with the theoretical value is very satisfactory. For the temperatures 77.95 and 71.92° K. there is a

---

¹) S. DÄUMICHEN, Zs. f. Phys. **62**, 414, 1930.

²) F. RASETTI, Proc. Nat. Acad. Amer. **15**, 515, 1929.

discrepancy of which we cannot find, what experimental error could have caused it. We observe that for oxygen a similar discrepancy was found [1]).

In Fig. 1 we also plotted the velocity of sound in the ideal gas, with $(c_p/c_v)_{p=0} = 1.400$ (indicated by ◈).

§ 5. *Calculation of the dependence of the second virial coefficient B on the temperature.*

We calculated a curve $B = f(1/T)$ of the fourth degree in $1/T$ from the following data on B and S (comp. equation (2)):

$$\begin{array}{ll} T = 77.95\ {}^\circ\mathrm{K}. & 10^3 . S = -7.291 \\ T = 90.37 & 10^3 . S = -4.919 \\ T = 126.77 & 10^3 . B = -4.542 \\ T = 140.00 & 10^3 . S = -1.726 \\ T = 151.90 & 10^3 . B = -3.117 \end{array} \left. \vphantom{\begin{array}{l} T \\ T \\ T \end{array}} \right\} {}^{2)}$$

We found:

$$10^3\, B = -4.090 + \frac{24.627}{T}\, 10^2 - \frac{57.319}{T^2}\, 10^4 + \frac{41.159}{T^3}\, 10^6 - \frac{11.403}{T^4}\, 10^8 . \quad (3)$$

We took $\lambda = 5/2$ also at the lowest temperatures. From this formula we calculated values of S and B (table XI). The first have been plotted in Fig. 2 (indicated by ×).

TABLE XI.

T °K.	$10^3 . S$	$10^3 . B$
70	−9.961	−13.382
80	−6.787	−10.319
90	−4.971	− 8.411
100	−3.813	− 7.026
110	−3.022	− 5.937
120	−2.455	− 5.052
130	−2.038	− 4.322
140	−1.727	− 3.711
150	−1.492	− 3.204

---

[1]) W. H. KEESOM, A. VAN ITTERBEEK and J. A. VAN LAMMEREN. These Proceedings **34**, 1001, 1931. Comm. Leiden No. 216*d*.

[2]) The values of B were derived from measurements of KAMERLINGH ONNES and VAN URK. loc. cit. We calculated the value of S at $T = 140°$ K. from B-values in this temperature range.

In Fig. 3 the B-points following from our formula are indicated by $\triangle$.

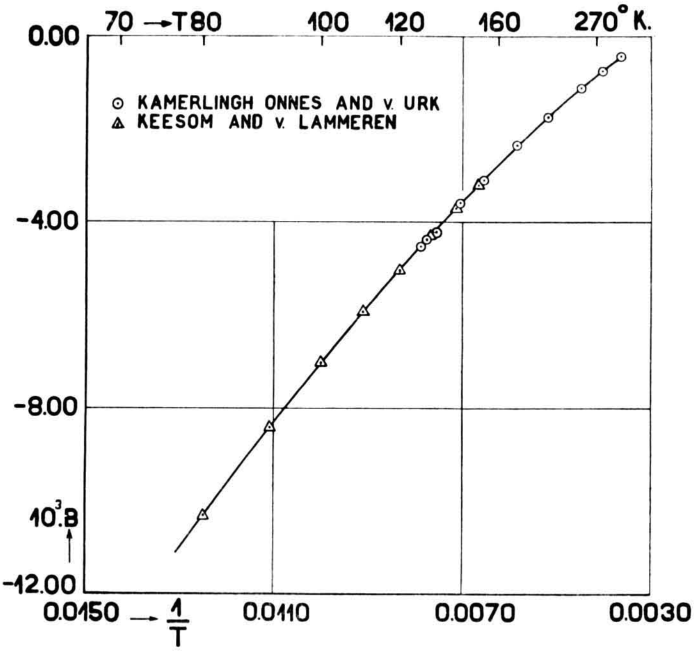

Fig. 3

§ 6. *Calculation of the ratio c_p/c_v and the specific heats themselves.* Deriving B and dB/dT from the formula (3) mentioned above and the third virial coefficient C by means of "the average empirical reduced equation of state" ¹) we calculated c_p/c_v, c_p and c_v at the temperatures 90.37 and 82.95° K. W was calculated from the coefficients W_0 and s (§ 4). The formulas used have been published by A. VAN ITTERBEEK ²). The results are shown in table XII.

TABLE XII.

T °K.	Pressure at	c_p cal/mole	c_v cal/mole	c_p / c_v
90.37	0.0	6.94	4.96	1.400_7
	0.3	7.01	4.97	1.409_7
	0.6	7.08	4.99	1.419_1
	0.9	7.15	5.00	1.428_9
82.95	0.0	6.94	4.96	1.400_5
	0.3	7.05	5.00	1.411_0
	0.6	7.15	5.03	1.422_1
	0.9	7.25	5.08	1.433_9

---

¹) H. KAMERLINGH ONNES and W. H. KEESOM, Encycl. d. Math. Wiss. V **10**, 615, 1912. Comm. Leiden Suppl. No. **23**, 117, 1908.

²) A. VAN ITTERBEEK, Wis- en Nat. Tijdschr. **5**, 192, 1932. Comm. Leiden Suppl. N⁰. 70*b*.

For comparison we refer to the value of c_p found by SCHEEL and HEUSE [1]) being 7.162 at the temperature 92° K. and a pressure of about one atmosphere.

We gladly record our thanks to Mr. W. BEVELANDER, phil. nat. cand., for his assistance in this investigation.

Summary.

The velocity of sound in nitrogen gas has been measured in the temperature range extending from 0° C. down to liquid nitrogen temperatures, in dependence on the pressure. Four resonators are used to get an idea of the validity of the formula of KIRCHHOFF-HELMHOLTZ. This formula proves to give good results. A curve $B = f(1/T)$ (B being the second virial coefficient) has been calculated holding from 150 down to 80° K. Also the ratio c_p/c_v and the specific heats c_p and c_v were calculated.

---

[1]) K. SCHEEL and W. HEUSE, Ann. d. Phys. (4) **40**, 473, 1913.

Physics. — *On the Anomaly in the Specific Heat of Liquid Helium.* By W. H. KEESOM and Miss A. P. KEESOM. Communication N⁰. 221*d* from the KAMERLINGH ONNES Laboratory at Leiden.

(Communicated at the meeting of June 25, 1932).

§ 1. *Introduction.* The investigation on the specific heat of liquid helium made by one of us with Dr. CLUSIUS [1]) gave rise to some questions which made a nearer investigation of the anomaly of the specific heat of that substance, revealed by the investigation mentioned, desirable.

So it seemed important to see whether the curve of the specific heats obtained should undergo some change if a better heat conduction in the liquid was provided for. In this connection the course of the curve of the specific heats above 2.19° K attracted special attention. Although we have not yet been able to make experiments in which the conditions of heat supply and heat conduction were the most ideal ones, we could make some measurements with improved heat conduction in the liquid in such a way that we can draw at least a preliminary conclusion concerning this question.

---

[1]) W. H. KEESOM and K. CLUSIUS. These Proceedings, **35**, 306. 1932; Comm. Leiden No. 219*e*.