Physics. - Measurements about the velocity of sound in oxygen gas. By W. H. Keesom, A. van Itterbeek and J. A. van Lammeren. (Communication $\mathrm{N}^{0} .216 d$ from the Physical Laboratory at Leiden).
(Communicated at the meeting of September 26, 1931.)
§ 1. Introduction. Measurements about the velocity of sound in oxygen at low temperatures were only done till now by Cook ${ }^{1)}$ at temperatures obtained with liquid air. He used the Kundt's method. We estimated it to be interesting to measure the velocity of sound in the whole temperature range from $0^{\circ} \mathrm{C}$ down to $-196^{\circ} \mathrm{C}$, by using our more accurate method, elaborated and applied to helium ${ }^{2}$ ) and hydrogen ${ }^{3}$ ) in our previous communications.

As explained in previous communications, such accurate measurements enable us to draw conclusions about the ratio of the specific heats at constant pressure and constant volume and also about the second virial coefficient. Concerning these values other experimenters have already performed measurements. Scheel and Heuse ${ }^{4}$ ) determined $c_{p}$, by a calorimetrical method, at the temperatures - $76^{\circ} \mathrm{C}$ and $-181^{\circ} \mathrm{C}$. Nijhoff and Keesom ${ }^{5}$ ) determined the second virial coefficient $B$ at temperatures of liquid ethylene, Cath and Kamerlingh Onnes ${ }^{6}$ ) deduced values of $B$ down to $-189^{\circ} \mathrm{C}$ from measurements of the pressure coefficient.

The measurements, treated in this communication, enabled us to calculate $c_{p}, c_{v}, c_{p} / c_{v}$ and $\left(c_{p} / c_{v}\right)_{p=0}$ over the whole temperature range mentioned and moreover to deduce a relation between $B$ and the temperature in a range extending from liquid ethylene down to liquid oxygen temperatures.
§ 2. Method and apparatus. We followed the method described in Comm. N ${ }^{0} .213 b^{2}$ ). To determine the temperature we used a platinum resistance thermometer.

The oxygen was obtained by fractional evaporation of commercial pure oxygen.

[^0]
## § 3. Experimental results.

a. Measurements at $0^{\circ} \mathrm{C}$. The results of these measurements are given in Table I.

TABLE I.

| Velocity of sound in oxygen at $0^{\circ} \mathrm{C}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Resonator | Diam. <br> mm | Length <br> $0^{\circ} \mathrm{C} \mathrm{mm}$ | $W_{\text {obs }}$ <br> average <br> $\mathrm{m} / \mathrm{sec}$ | $W$ <br> $\mathrm{~m} / \mathrm{sec}$ |
| $R_{I}$ | 25.9 | 301.4 | 314.0 | $\} 315.4$ |
| $R_{I I}$ | 62.0 | 297.7 | 314.8 | 315 |

In this table $W_{\text {obs }}$ means the average value obtained from several observations and $W$ the velocity of sound corrected for the influence of the wall. This correction was made by means of an extrapolation to an infinite diameter, based on the measurements in both resonators $R_{I}$ and $R_{I I}{ }^{1}$ ).

Scheel and Heuse ${ }^{2}$ ) and Schweikert ${ }^{3}$ ) found respectively for the velocity of sound the values 315.2 and $315.8 \mathrm{~m} / \mathrm{sec}$. We see that our value 315.4 agrees with theirs.
b. Measurements at temperatures of liquid ethylene. The results of these measurements we give in Table II.

TABLE II (July 14th, 1931).

| Velocity of sound in oxygen at liquid <br> ethylene temperatures |  |  |  |
| :---: | :---: | :---: | :---: |
| $T$ <br> ${ }^{\circ} \mathrm{K}$ | Pressure <br> at | $W_{\text {obs }}$ <br> average <br> $\mathrm{m} / \mathrm{sec}$ | $W$ <br> $\mathrm{~m} / \mathrm{sec}$ |
| 164.63 | 0.9075 | 244.0 | 244.3 |
| 160.61 | 0.8930 | 240.7 | 2410 |
| 15579 | 0.8747 | 237.1 | 237.4 |
| 144.84 | 0.8311 | 228.7 | 229.0 |

These measurements ${ }^{4}$ ) were done by means of the wide resonator $R_{I I}$.

[^1]We calculated the velocity of sound for the free gas from the observed one according to the method applied in Comm. Nos. 209a, c and $213 b$.
c. Measurements at temperatures of liquid oxygen. In this temperature range we measured the dependency of the velocity of sound on pressure. The results are given in Table III.

TABLE III.

| Velocity of sound in oxygen at liquid oxygen temperatures Resonator RII. |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Date of the measurement | ${ }_{{ }^{\circ} \mathrm{K}}^{T}$ | Pressure at | $\begin{gathered} W_{\text {obs }} \\ \text { average } \\ \text { m/sec } \end{gathered}$ | $\underset{\mathrm{m} / \mathrm{sec}}{W}$ |
| July 3rd, 1931 | 90.00 | 0.8453 | 178.2 | 178.3 |
| 8 th . | $\cdots$ | 0.6732 | 178.8 | 178.9 |
| 3rd. | * | 0.3981 | 179.9 | 180.0 |
| 8th, .. | * | 0.1713 | 180.8 | 181.0 |
| June 11th, 1931 | 86.27 | 0.5202 | 175.2 | 175.3 |
| July 3rd. | " | 0.4680 | 175.4 | 175.5 |
| June 12th, | " | 0.4373 | 175.6 | 175.7 |
| . 12th, .. | " | 0.3473 | 176.0 | 176.2 |
| July 3rd, | " | 0.2979 | 176.1 | 176.3 |
| June 12th, | " | 0.2822 | 176.3 | 176.4 |
| July 3rd. | " | 0.2040 | 176.5 | 176.6 |
| June 12th, | " | 0.1552 | 176.9 | 177.1 |
| June 13th, 1931 | 83.80 | 0.3932 | 172.8 | 172.9 |
| . 13th, | " | 0.3368 | 173.2 | 173.4 |
| . 13th, . | " | 0.2674 | 173.5 | 173.6 |
| July 8th, .. | - | 0.2102 | 173.8 | 173.9 |
| June 13th, .. | - | 0.2008 | 173.7 | 173.8 |
| .. 13th. - | " | 0.1384 | 174.0 | 174.2 |
| July 8th, | * | 0.1295 | 174.1 | 174.3 |
| July 9th. 1931 | 77.48 | 0.1915 | 166.6 | 166.7 |
| .. 9th, .. | * | 0.1447 | 167.1 | 167.3 |
| ." 9th. . | " | 0.1035 | 167.3 | 167.5 |

In Fig. 1 we plotted $W$ as a function of $p$.


Fig. I.
$\nabla$ June 12th, $\odot$ June 13th, $\triangle$ July 3rd, $\odot$ July 8th, $\odot$ July 9th.
We observe that the variation with pressure is small compared with that obtained for helium and hydrogen.

The value 173.9 observed by Cook ${ }^{1}$ ) for the velocity of sound at the temperature $-183^{\circ} \mathrm{C}$, and the pressure 0.657 at. is smaller than ours, under the same conditions.
§ 4. Calculations. a. $0^{\circ} \mathrm{C}$. By means of the formulas mentioned in Comm. $\mathrm{N}^{0}$. 209c, we calculated from $W$ the values $c_{p} / c_{v},\left(c_{p} / c_{v}\right)_{p=0}, c_{p}$ and $c_{v}$. We deduced the terms $B, d B / d T$ and $d^{2} B / d T^{2}$, wanted in this calculation, from a quadratic formula $B=f(1 / T)$, calculated by means of known values of $B$ at the neighbourhood of $0^{\circ} C$. These values were derived from Nijhoff and Keesom ${ }^{2}$ ).

[^2]Table IV gives the results.
TABLE IV.
$0^{\circ} \mathrm{C}$.

| Pressure <br> at | $c_{p}$ <br> $\mathrm{cal} /$ mole | $\mathbf{c}_{v}$ <br> $\mathrm{cal} / \mathrm{mole}$ | $\mathrm{c}_{p} / \mathrm{c}_{\boldsymbol{p}}$ | $\left(\mathrm{c}_{p} / \mathrm{c}_{v}\right)_{p=0}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0.985 | 6.98 | 4.97 | 1.404 | 1.402 |

b. Temperatures of liquid ethylene. We calculated $c_{p} / c_{v},\left(c_{p} / c_{v}\right)_{p=0}$, $c_{p}$ and $c_{v}$ in the same way as at the temperature $0^{\circ} \mathrm{C}$.

The values of $B, d B / d T$ and $d^{2} B / d T^{2}$ we deduced from the formula

$$
10^{3} B=+1.93-\frac{580}{T}-\frac{4.50 \cdot 10^{4}}{T^{2}}
$$

laid through known values of $B$ at these temperatures.
For the results see Table V :

TABLE V.
Liquid Ethylene Temperatures.

| $T$ <br> ${ }^{\circ} \mathrm{K}$ | Pressure <br> at | $c_{p}$ <br> $\mathrm{cal} / \mathrm{mole}$ | $c_{v}$ <br> $\mathrm{cal} / \mathrm{mole}$ | $c_{p} / c_{v}$ | $\left(c_{p} / c_{v}\right)_{p=0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 164.83 | 0.9075 | 7.00 | 4.96 | 1.408 | 1.401 |
| 160.61 | 0.8930 | 7.03 | 5.00 | 1.406 | 1.398 |
| 155.79 | 0.8747 | 7.02 | 4.99 | 1.407 | 1.399 |
| 144.84 | 0.8311 | 6.99 | 4.96 | 1.411 | 1.402 |

It appears that the ratio $\left(c_{p} / c_{v}\right)_{p}=0$ is constant within the limits of accuracy and equal to 1.400 .
c. Temperatures of liquid oxygen. It proves to be possible to represent the observed data of table III at the temperatures $90.00^{\circ} \mathrm{K}$ and $86.27^{\circ} \mathrm{K}$ by a quadratic formula of the form ${ }^{1}$ )

$$
W^{2}=N\left(1+P p+Q p^{2}\right)
$$

and those at the temperatures $83.80^{\circ} \mathrm{K}$ and $77.48^{\circ} \mathrm{K}$ by a linear formula in $p$. We calculated the coefficients $N, P$ and $Q$ with the method of least squares.

[^3]Further we calculated the ratio $\left(c_{p} / c_{p}\right)_{p=0}$ from the coefficient $N$. From the coefficient $P$ we deduced the values of

$$
S=\frac{1}{2} R T \cdot P=B+\frac{1}{\lambda} T \frac{d B}{d T}+\frac{1}{2 \lambda(\lambda+1)} T^{2} \frac{d^{2} B}{d T^{2}}
$$

For the results of these calculations see table VI ${ }^{1}$ ).
TABLE VI.

| $T$ <br> ${ }^{\circ} \mathrm{K}$ | $N$ <br> $\mathrm{~m} / \mathrm{sec})^{2}$ | $P$ <br> $\mathrm{at}-1$ | $Q$ <br> at-2 | $S .10^{3}$ | $\left(c_{p} / c_{\nu}\right)_{p=0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 90.00 | 33027 | -0.04948 | 0.006170 | -8.15 | 1.412 |
| 86.27 | 31597 | -0.05623 | 0.007689 | -8.88 | 1.409 |
| 83.80 | 30567 | -0.05250 | - | -8.05 | 1.404 |
| 77.48 | 28353 | -0.09902 | - | -14.04 | 1.408 |

We observe that the values of $\left(c_{p} / c_{v}\right)_{p=0}$ are a little greater than 1.400 . This fact might express, that the rotational energy is not completely excited. However, if we calculate the rotational energy by means of the formulas ${ }^{2}$ ) deduced for it, we find, that at liquid oxygen temperatures this energy has already reached its full value. About the question whether the rotational energy shows deviations from the classical value or not, we cannot conclude from our measurements.

In a previous communication ${ }^{3}$ ) we indicated how it is possible to establish from measured values of $S$ together with known values of $B$, a function of $B$ with temperature.

From the value of $B$ at the temperature $120.53^{\circ} \mathrm{K}$, the value of $\frac{d B}{d T}$ at the temperature $123.10^{\circ} \mathrm{K}$, calculated from measured values of $B$ in this temperature range, and from an average of the two measured values of $S$ at the two highest temperatures we calculated the quadratic formula

$$
\begin{equation*}
10^{3} \cdot B=-36.45+\frac{8947}{T}-\frac{63.62}{T^{2}} 10^{4} \tag{1}
\end{equation*}
$$

For comparison we give in table VII the values of $S$ measured and the values of $S$ calculated from the formula (1).

[^4]TABLE VII.

| $T$ <br> ${ }^{\circ} \mathrm{K}$ | $10^{3} S$ <br> measured | $10^{3} S$ <br> calculated |
| :---: | :---: | :---: |
| 90.00 | -8.15 | -8.18 |
| 86.27 | -8.88 | -8.84 |
| 83.80 | -8.05 | -9.43 |
| 77.48 | -14.04 | -11.52 |

In table VIII we mentioned a series of values of $B$ calculated from the formula (1).

TABLE VIII.
Values of $B$.

| $T$ <br> ${ }^{\circ} \mathrm{K}$ | $1^{10^{3} B}$ |
| :---: | :---: |
| 110 | -7.70 |
| 100 | -10.60 |
| 90 | -15.58 |
| 85 | -19.25 |

From the formula (1) it follows that at a temperature $T=90.12^{\circ} \mathrm{K}$

$$
10.3^{3} B=-15.50,
$$

calculated by means of the formula of Clapeyron ${ }^{1}$ ) $=-15.91$,
,. by Cath and Kamerlingh Onnes 2) =-10.6,
,. by means of the "average empirical
reduced equation of state" ${ }^{3}$ ) $=-16.87$.

By means of the values of $B, d B / d T$, and $d^{2} B / d T^{2}$ according to the formula mentioned above we calculated $c_{p} / c_{v}, c_{p}, c_{v}$ for several temperatures and pressures, see table IX.

[^5]TABLE IX.

| $T$ <br> ${ }^{\circ} \mathrm{K}$ | Pressure <br> at | $c_{p}$ <br> $\mathrm{cal} / \mathrm{mole}$ | $c_{v}$ <br> $\mathrm{cal} / \mathrm{mole}$ | $c_{p} / c_{v}$ |
| :---: | :---: | :---: | :---: | :---: |
| 90.00 | 0.0 | 6.80 | 4.82 | 1.412 |
| 0.5 | 7.64 | 5.27 | 1.449 |  |
|  | 0.9 | 8.32 | 5.60 | 1.485 |
| 86.27 | 0.0 | 6.84 | 4.85 | 1.409 |
| 83.80 | 0.3 | 7.42 | 5.16 | 1.437 |
|  | 0.6 | 8.01 | 5.45 | 1.470 |
|  | 0.2 | 6.90 | 4.92 | 1.404 |
|  | 0.4 | 7.74 | 5.33 | 1.452 |

We find the specific heat $c_{p}$ to be equal to $8.40 \mathrm{cal} / \mathrm{mole}$ at the temperature $90^{\circ} \mathrm{K}$ and the pressure 0.95 at, whereas the value, found by Scheel and Heuse, was 7.30 at the temperature $92^{\circ} \mathrm{K}$ and at the same pressure.

We thankfully acknowledge that this research was furthered by a grant from the "Fonds National de la Recherche scientifique" of Belgium.

## Summary.

In this communication we related about measurements of the velocity $W$ of sound in oxygen at $0^{\circ} \mathrm{C}$, at liquid ethylene temperatures, and at liquid oxygen temperatures.

From the measurements at $0^{\circ} \mathrm{C}$ (Table I) and at liquid ethylene temperatures (Table II) we calculated $c_{p}, c_{v}, c_{P} / c_{v}$, and $\left(c_{p} / c_{v}\right)_{p=0}$ (Table IV and V). At liquid oxygen temperatures we measured the dependency of the velocity of sound on pressure (Table III). We found that it was possible to represent these observations by means of the formula $W^{2}=$ $N\left(1+P p+Q p^{2}\right)$ (Table VI). From the coefficient $N$ we calculated $\left(c_{P} / c_{v}\right)_{p=0}$. From these measurements we deduced also a formula for $B$ as function of $T$ for the temperature range from $137^{\circ} \mathrm{K}$ down to $86^{\circ} \mathrm{K}$. A list of values of $B$ is given in table VIII. With the given formula for $B$ we calculated $c_{p}, c_{v}, c_{p} / c_{v}$ (Table IX).


[^0]:    ${ }^{1}$ ) S. R. Соок, Phys. Rev. 23, 212, 1906.
    ${ }^{2}$ ) W. H. Кeesom and A. van Itterbeek, These Proceedings : 33, 440, 1930; 34, 204, 1931; Comm. Leiden Nos. 209a and 213b. A. van Itterbeek and W. H. Keesom, Wis- en Natuurk. Tijdschrift 5, 69, 1930; Comm. Leiden, №. 209c.
    ${ }^{3}$ ) A. van Itterbeek and W. H. Keesom, These Proceedings 34, 988, 1931 ; Comm. Leiden $\mathrm{N}^{0}$. 216 c .
    ${ }^{4}$ ) K. Scheel and W. Heuse. Ann. d. Phys. (4), 40. 473, 1913.
    ${ }^{5}$ ) G. P. NiJhoff and W. H. Keesom, These Proceedings: 28, 963, 1925; Comm. Leiden №. $179 b$.
    ${ }^{6}$ ) P. G. Cath and H. Kamerlingh Onnes, Arch. Néerl. sér. IIIa. 6. 1, 1922 ; Comm. Leiden, No. 156 a .

[^1]:    ${ }^{1}$ ) E. Grüneisen and E. Merkel. Ann. d. Phys. (4), 66, 352, 1921.
    ${ }^{2}$ ) loc. cit.
    ${ }^{3}$ ) G. Schweikert. Ann. d. Phys. (4), 48. 590, 1915.
    ${ }^{4}$ ) At these measurements we have operated with the same quantity of gas, so that we can consider the density to be constant in first approximation, because there was only a small percentage of the gas in the connecting tubes at room temperature.

[^2]:    $\left.{ }^{1}\right)$ loc. cit.
    ${ }^{2}$ ) loc. cit.

[^3]:    ${ }^{1}$ ) Compare Comm. Leiden Nos. $213 b$ and $216 c$.

[^4]:    ${ }^{1}$ ) For the meaning of $\lambda$ see Comm. Leiden Nos. 209c, 213b, 216 c.
    ${ }^{2}$ ) See e.g. H. Beutler, Zs. f. Phys. 50, 598, 1928. For the value of the moment of inertia we took $I=19,20.10^{-40}$ (W. Ossenbrüggen, Zs. f. Phys. 49, 167, 1928).
    $\left.{ }^{3}\right)$ Comm. Leiden $\mathrm{N}^{0} .216 c$.

[^5]:    ${ }^{1}$ ) For the method used for these calculations, cf. M. C. Johnson Proc. Phys. Soc. 42, 170, 1930. Dr. W. Tuyn was so kind to give us this result, which he calculated for an other purpose.
    ${ }^{2}$ ) loc. cit.
    ${ }^{3}$ ) H. Kamerlingh Onnes and W. H. Keesom. Encycl. d. Math. Wiss. V 10, 615, 1912. Comm. Leiden, Suppl. No. 23, 117, 1908.

