

Physics. — Isothermals of helium at temperatures of 0, 20 and 100° C., and pressures from 5,5 to 16,5 atmospheres. By W. H. KEESOM and J. J. M. VAN SANTEN. (Communication No. 227*b* from the KAMERLINGH ONNES Laboratory at Leiden).

(Communicated at the meeting of September 30, 1933.)

Summary. For the sake of thermometry, especially for a more accurate ascertaining of the position of the ice point on the KELVIN-scale, it was resolved some years ago that very careful redeterminations should be made, of the fundamental pressure coefficient of helium on the one hand, of the isothermals of helium at 0° and 100° C. on the other hand. This paper contains the results of the last mentioned investigation. They are:

$$B_{0^{\circ}\text{C.}} = 0.5028 \times 10^{-3}, \quad B_{20^{\circ}\text{C.}} = 0.4989 \times 10^{-3}, \quad B_{100^{\circ}\text{C.}} = 0.4814 \times 10^{-3}.$$

The value $B_{100^{\circ}\text{C.}} - B_{0^{\circ}\text{C.}} = -0.0214 \times 10^{-3}$ is estimated to have a mean error $\pm 0.005 \times 10^{-3}$.

§ 1. *Introduction.* The position of the ice-point (0° C.) on the KELVIN-scale can be derived from measurements with the gasthermometer of the pressure coefficient between 0° and 100° C. (the fundamental temperature interval), and from measurements of the compressibility of the gas used at the temperatures mentioned, *i. e.* of measurements of isothermals. As for helium the difference between the fundamental pressure coefficient $\alpha_{n\text{He}}$ and the fundamental temperature coefficient α_A is smallest, helium is mostly indicated for investigations on that fundamental constant of thermometry. So it was decided some years ago that for a more accurate determination of the position of the ice point on the KELVIN-scale very careful redeterminations should be made, of the fundamental pressure coefficient of helium on the one hand, of the isothermals on the other hand. The investigation on the fundamental pressure coefficient of helium is still going on. Preliminary results were published¹⁾. The results of the measurements on the isothermals are given in this paper.

§ 2. The fundamental pressure coefficient is by definition:

$$\alpha_{n\text{He}} = \frac{p_{100^{\circ}\text{C.}} - p_{0^{\circ}\text{C.}}}{p_{0^{\circ}\text{C.}} \cdot 100}, \quad \dots \dots \dots (1)$$

$p_{0^{\circ}\text{C.}}$, the icepoint pressure of the gasthermometer, being $100/76 \times$ the normal atmosphere²⁾).

¹⁾ W. H. KEESOM and Miss H. VAN DER HORST. These Proceedings 30, 970, 1927, Comm. Leiden N^o. 188*a*; W. H. KEESOM, A. BIJL and Miss H. VAN DER HORST. These Proceedings 34, 1223, 1931, Comm. Leiden N^o. 217*a*, § 3.

²⁾ At Leiden 75.9529 cm mercury, cf. Comm. Leiden Suppl. N^o. 51*a*, p. 11, note 1.

With sufficient accuracy the fundamental temperature coefficient α_A is derived from it by

$$\alpha_A = \alpha_{nHe} - (1 + 100 \alpha_A) \frac{100}{76} \cdot \frac{B_{100^\circ C.} - B_{0^\circ C.}}{100} \dots \dots (2)$$

$B_{0^\circ C.}$ and $B_{100^\circ C.}$ are the second virial coefficients of KAMERLINGH ONNES' equation of state in the form:

$$p v_A = A_A \left(1 + \frac{B}{v_A} + \frac{C}{v_A^2} \dots \right) \dots \dots (3a)$$

The B 's are related with the B_A 's of the equation

$$p v_A = A_A + B_A d_A + C_A d_A^2 \dots, d_A = v_A^{-1}, \dots \dots (3b)$$

by $B = B_A/A_A$.

In these equations p is measured in normal atmospheres, v_A is the volume in terms of the normal volume ($0^\circ C.$, 1 atm.).

For determining B it is most advisable to measure isothermals in that range of densities in which on the one hand C does not have an appreciable influence, and on the other hand the term with B is large enough to allow a sufficiently accurate calculation of B ¹⁾. We made measurements in the range of d_A from 4,5 to 12,5.

In this range the term $C_A d_A^2$ has a maximum value of about 0,00002 ²⁾ and can be neglected, so that instead of equations (3) we may write

$$p v_A = A_A \left(1 + \frac{B}{v_A} \right), \dots \dots (4a)$$

$$p v_A = A_A + B_A d_A \dots \dots (4b)$$

§ 3. *The experiments.* For the method and the apparatus we refer to previous publications ³⁾. A report on some improvements made in the course of this investigation was given by one of us elsewhere ⁴⁾.

The helium, obtained by evaporation of liquid helium and tested spectroscopically, was contained in a bulb of Jena thermometer glass 2954 III, capacity 40 cm³, connected through a capillary with a cylin-

¹⁾ Cf. G. P. NIJHOFF and W. H. KEESOM. These Proceedings 28. 963, 1925. Comm. Leiden N^o. 179b, § 1.

²⁾ Calculated from $C_{A0^\circ C.} = 0,12 \cdot 10^{-6}$, $C_{A100^\circ C.} = 0,16 \cdot 10^{-6}$. H. KAMERLINGH ONNES. Comm. N^o. 102a. If we should use the german values of C_A , the maximum value of $C_A d_A^2$ would be 0,00004. The value of our B 's, table IV, must then be diminished with $0,0020 \cdot 10^{-3}$, $B_{100^\circ C.} - B_{0^\circ C.}$ remains unchanged.

³⁾ H. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN. These Proc. 3, 621, 1901, Comm. N^o. 69; J. C. SCHALKWIJK, These Proc. 4, 23, 1902, Comm. N^o. 70; H. KAMERLINGH ONNES and C. BRAAK. These Proc. 9, 754, 1907, Comm. N^o. 97a; H. A. KUYPERS and H. KAMERLINGH ONNES. Arch. Néerl. (IIIA) 6, 277, 1923, Comm. N^o. 165a; G. P. NIJHOFF and W. H. KEESOM. These Proc. 31, 404, 1928, Comm. N^o. 188b.

⁴⁾ J. J. M. VAN SANTEN. Wis- en Nat. Tijdschr. 6, 59, 1932. Comm. Leiden N^o. 227a.

dricul glass tube, into which mercury could be pressed, and which was kept at 20° C. The quantity of gas in the bulb was calculated by subtracting from the total quantity the quantity of gas contained in the cylindrical tube (the stem) and the connection. For this purpose the isothermal of 20° C. was determined.

The total quantity was determined by measuring the normal volume. The pressure was measured with a closed manometer, which was compared with the absolute manometer.

0° C. was realised by means of melting ice in equilibrium with air-saturated distilled water, 100° C by means of steam from distilled water, a correction being applied for the deviation of the pressure from the normal atmosphere. For this purpose a new steam point apparatus was built after the design previously described ¹⁾ with some slight improvements.

§ 4. *Volume of mercury menisci.* A serious difficulty was caused by the volume of the mercury meniscus in the piezometer stem, whose average radius was 0.587 cm. Mercury menisci volumes for tubes of about this dimension have been measured by PALACIOS²⁾ only. For the average height of our menisci, 0.140 cm, we take from his results $v = 98.0 \text{ mm}^3$.

For larger radii SCHEEL and HEUSE³⁾ have measured menisci volumes. Their results are systematically about 11 mm³ smaller than PALACIOS' values for those radii. By extrapolating SCHEEL and HEUSE's values one should expect for $r = 0.587$ a volume, 8.5 mm³ smaller than PALACIOS' number.

In view of this difference and the high importance the exact knowledge of the menisci volumes has for different researches of high accuracy, in this laboratory an elaborate investigation has been taken in hand in which an X-ray shadowgraph of the meniscus is measured. For $r = 0.587$ cm the measurements have been completed: for $h = 0.140$ cm a value of v was found 5.1 mm³ smaller than PALACIOS' value ⁴⁾.

We checked this result by another method. A tube with radius 0.587 cm was connected with an accurately calibrated capillary and filled with very pure mercury. By cautiously changing the pressure above the mercury in the capillary the height of the meniscus in the other tube could be changed, the rim of the meniscus remaining unchanged. So we could measure the differences in volume of menisci from $h = 0.050$ to $h = 0.170$ cm. As an average from 12 series of measurements we found those

¹⁾ W. H. KEESOM and Miss H. VAN DER HORST. These Proc. **30**, 970, 1927. Comm. No. 188a, fig. 1.

²⁾ J. PALACIOS. Ann. Soc. Esp. de Fis. y Quim. **17**, 275, 1919; Phys. Zs. **24**, 151, 1923.

³⁾ K. SCHEEL and W. HEUSE. Ann. d. Phys. (4) **33**, 295, 1910.

⁴⁾ We gladly record our thanks to Miss H. VAN DER HORST, phil. nat. doct^a and Mr. K. W. TACONIS, phil. nat. cand., for their important help in providing us with this number.

differences 6.6 mm^3 smaller than PALACIOS. By extrapolating to $h=0$ a difference with PALACIOS of 7.6 cm^3 would follow. In taking a weighted mean between this result and that furnished by the X-ray method, we assume 6.2 mm^3 , so that for $r=0.587$ and $h=0.140 \text{ cm}$, the meniscus volume is accepted to be $91.8 \pm 1.2 \text{ mm}^3$.

As the heights of the different menisci were nearly the same, we applied for all of them the same correction to PALACIOS' values.

§ 5. *The accuracy* of the $p\nu_A$'s is about 1 : 10000. This gives a mean error of about $0,010 \cdot 10^3$ in the values of B . This resulting error is principally dependent on small accidental errors in the volume and pressure calibrations.

Errors in the temperatures 0° and 100° C. , or in the thermal expansion coefficient of glass ¹⁾ are too small to have an appreciable influence on the result. As still remaining errors in the estimation of the volume of the mercury menisci (§ 4) partly cancel one another, the resulting value of $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}$ is more accurate than $0,010 \cdot 10^{-3}$, mentioned above. The estimated mean error in $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}$ is $0,005 \cdot 10^{-3}$, corresponding with an error of 0,005 degree in the fundamental interval, of $0,9 \times 10^{-7}$ in α_A , or of 0,007 in $T_{0^\circ\text{C.}}$.

§ 6. *The results* of the isothermal measurements are collected in table I—III. The values $p\nu_{A_{\text{calc.}}}$ were calculated with the values of the virial coefficients given in § 7.

Each experimental point is the result of 4 complete measurements, for the 100° C. isothermal several points even of 6 measurements.

§ 7. *The second virial coefficients.* For calculating the values of B the normal volume point was added to each isothermal as given in the tables I—III. For practical reasons the normal volume had been measured at 18° C. and 1 atm. The most accurate method for reduction to 0° C. is by means of the expansion coefficient $\alpha_p^{0-18^\circ\text{C.}}$. The result was:

before the isothermal measurements: 548.834 cm^3 .
 after " " " : 548.888 "
 average 548.861 ± 0.027

The most accurate reduction to 100° C. is obtained by starting from the 0° C. value and calculating with the pressure coefficient $\alpha_p^{0-100^\circ\text{C.}}$ at 1 atm. So for the normal volume points in terms of the normal volume we took

	p	d_A	$p\nu_A$
0° C.	1	1	1
20° C.	1	1	$1 + 20 \alpha_p^{0-20^\circ\text{C.}}$
100° C.	$1 + 100 \alpha_p^{0-100^\circ\text{C.}}$	$1 + 20 \alpha_p^{0-20^\circ\text{C.}}$	$1 + 100 \alpha_p^{0-100^\circ\text{C.}}$

¹⁾ See the reference quoted note 4, p. 814.

TABLE I. Isothermal of helium for 20 °C.

Date	Nº.	p	d_A	$p\nu_A$ obs	$p\nu_A$ calc	$(O-C) \times 10^{+5}$
20 May 1932	1	5.56381	5.17472	1.07519	1.07543	- 24
	2	6.20789	5.77113	1.07568	1.07575	- 7
	3	7.00056	6.50508	1.07617	1.07614	+ 3
	4	8.02048	7.44873	1.07676	1.07665	+ 11
	5	9.36486	8.69399	1.07716	1.07732	- 16
	6	11.25379	10.43667	1.07829	1.07825	+ 4
	7	12.20866	11.31811	1.07868	1.07872	- 4
	8	13.20781	12.23975	1.07909	1.07921	- 12
21 May 1932	1	13.24637	12.27430	1.07920	1.07923	- 3
	2	12.22852	11.33568	1.07876	1.07873	+ 3
	3	21.24266	10.42416	1.07852	1.07824	+ 28
	4	9.28986	8.62351	1.07727	1.07728	- 1
	5	8.03029	7.45662	1.07693	1.07665	+ 28
	6	7.00595	6.50940	1.07628	1.07615	+ 13
	7	6.21259	5.77497	1.07578	1.07575	+ 3
	8	5.56797	5.17842	1.07523	1.07543	- 20
24 May 1932	1	13.28507	12.31087	1.07913	1.07925	- 12
	2	12.22516	11.33350	1.07867	1.07873	- 6
	3	11.26387	10.44485	1.07841	1.07825	+ 16
	4	9.40695	8.73317	1.07715	1.07734	- 19
	5	8.03753	7.46413	1.07682	1.07666	+ 16
	6	7.02271	6.52494	1.07629	1.07615	+ 14
	7	6.21839	5.78038	1.07578	1.07576	+ 2
	8	5.57559	5.18583	1.07516	1.07544	- 28

For this calculation we accepted:

$$\alpha_p^{0-20^\circ\text{C.}} = \alpha_A + \frac{B_{20^\circ\text{C.}} - B_{0^\circ\text{C.}}(1 + 20\alpha_A)}{20} = 0,00365996 \dots \quad (5)$$

$$\begin{aligned} \alpha_v^{0-100^\circ\text{C.}} &= 0,0036609 \text{ for 1 m mercury } ^1) \\ &= 0,00366101 \text{ for 1 atm.} \end{aligned}$$

¹⁾ W. H. KEESOM, A. BIJL and Miss H. VAN DER HORST, l.c. p. 813, note 1.

TABLE II. Isothermal of helium of 0° C.

Date	N ^o	p	d_A	$p\nu_A obs$	$p\nu_A calc$	$(O-C)\times 10^{+5}$
26 May 1932	1	12.43204	12.36263	1.00561	1.00570	- 9
	2	11.48274	11.42075	1.00543	1.00522	+ 21
	3	10.65493	10.60214	1.00498	1.00481	+ 17
	4	8.98078	8.94453	1.00405	1.00398	+ 7
	5	7.69834	7.67063	1.00361	1.00334	+ 27
	6	6.76536	6.74596	1.00288	1.00287	+ 1
	7	6.01487	6.00120	1.00228	1.00250	- 22
27 May 1932	1	12.45699	12.38790	1.00558	1.00571	- 13
	2	12.46478	12.39543	1.00559	1.00571	- 12
	3	11.48867	11.42802	1.00531	1.00523	+ 8
	4	10.63712	10.58771	1.00467	1.00481	- 14
	5	8.94029	8.90267	1.00423	1.00396	+ 27
	6	7.70675	7.67917	1.00359	1.00334	+ 25
	7	6.75635	6.73732	1.00282	1.00287	- 5
	8	6.02039	6.00632	1.00234	1.00250	- 16
1 June 1932	1	6.05938	6.04541	1.00231	1.00252	- 21
	2	6.76787	6.74906	1.00279	1.00288	- 9
	3	7.71382	7.68803	1.00335	1.00335	0
	4	8.95584	8.92043	1.00397	1.00397	0
	5	10.64405	10.59301	1.00482	1.00481	+ 1
	6	11.50026	11.44048	1.00523	1.00523	0
	7	12.38806	12.32015	1.00551	1.00568	- 17

We then calculated the values of A_A and B_A according to equation (4b) by means of least squares, giving the normal volume points an appropriate weight¹⁾. The results are given in Table IV.

¹⁾ As the accuracy of the normal volume is about 1:20000, that of the individual points of the isothermals about 1:10000, we gave the normal volume points a weight 4, the 0° and 20° isothermal points the weight 1. In connection with the smaller densities of the gas in the bulb, which occurred at 100° C., we gave the 100° C. isothermal points a weight proportional to the density in the bulb and the corresponding normal volume point a weight 4 times that of the point at highest density.

TABLE III. Isothermal of helium of 100° C.

Date	N ^o .	<i>p</i>	<i>d</i> _A	<i>p</i> ^{<i>v</i>} _{A obs}	<i>p</i> ^{<i>v</i>} _{A calc}	(O-C)×10 ⁺⁵
12 May 1932	1	16.49988	12.01478	1.37330	1.37336	- 6
	2	15.03701	10.95345	1.37281	1.37266	+ 15
	3	13.55238	9.87678	1.37215	1.37196	+ 19
	4	10.92736	7.97280	1.37058	1.37070	- 12
	5	9.14228	6.67207	1.37023	1.36985	+ 38
	6	7.84993	5.73206	1.36948	1.36923	+ 25
	7	6.85434	5.00802	1.36867	1.36875	- 8
	8	6.08779	4.44879	1.36841	1.36839	+ 2
13 May 1932	1	16.53931	12.04401	1.37324	1.37338	- 14
	2	15.02817	10.94735	1.37277	1.37266	+ 11
	3	13.61973	9.92818	1.37182	1.37199	- 17
	4	10.94098	7.98359	1.37043	1.37071	- 28

§ 8. As one of us¹⁾ already communicated formerly, preliminary measurements had been made with small reservoirs of Thüringen glass. Isothermals of 100° C., however, could not be made with them, because of the bursting of the reservoirs by heating with steam. For different reasons the results obtained by these experiments have not quite the same accuracy as those dealt with above. We give the results in table V, as they can serve as a valuable check, diminishing the chance of systematic errors.

TABLE V.

	0° C.	20° C.
<i>A</i> _A	0.999583	1.07273
<i>B</i> _A	0.504 ⁶ .10 ⁻³	0.529 ⁴ .10 ⁻³
<i>B</i>	0.504 ⁸ .10 ⁻³	0.493 ⁵ .10 ⁻³

The agreement with the values of Table IV is very satisfactory. We consider those of table IV as the definitive ones.

¹⁾ Cf. p. 814 note 4.

TABLE IV, Virial coefficients of helium.

	0° C.	20° C.	100° C.
A_A	0.999485	1.072662	1.365465
B_A	$0.5025 \cdot 10^{-3}$	$0.5352 \cdot 10^{-3}$	$0.6573 \cdot 10^{-3}$
B	$0.5028 \cdot 10^{-3}$	$0.4989 \cdot 10^{-3}$	$0.4814 \cdot 10^{-3}$
$B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}} = -0.0214 \cdot 10^{-3}$			

§ 9. Comparison with previous results.

a. In view of the importance which the value of $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}$ has for thermometry (cf. § 2), and as the accuracy obtained for $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}$ is greater than that obtained for $B_{100^\circ\text{C.}}$ and $B_{0^\circ\text{C.}}$ separately, we compare the existing values of $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}$ in Table VI.

Relative to this table the following remarks are to be made.

KAMERLINGH ONNES calculated B from his measurements using estimated values of C . We recalculated the KAMERLINGH ONNES values using the values of C deduced from measurements by HOLBORN and OTTO²⁾.

For the Berlin values we chose the coefficients given by the authors

TABLE VI.

	$B_{0^\circ\text{C.}} \times 10^3$	$B_{100^\circ\text{C.}} \times 10^3$	$(B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}}) \cdot 10^3$
KAMERLINGH ONNES ¹⁾	0.505 ⁶	0.484 ¹	-0.021 ⁵
HOLBORN and OTTO ²⁾	0.529	0.513	-0.016
WIEBE, GADDY and HEINS ³⁾	0.521 ⁷	0.504 ⁴	-0.017 ³
KEESOM and VAN SANTEN	0.502 ⁸	0.481 ⁴	-0.021 ⁴

mentioned for a series in powers of v^{-1} , recalculating them for our unit of pressure. If one starts from the coefficients in powers of p ⁴⁾ one obtains:

HOLBORN and OTTO: $B_{0^\circ\text{C.}} = 0.529 \times 10^{-3}$, $B_{100^\circ\text{C.}} = 0.508 \times 10^{-3}$,
 $B_{100^\circ\text{C.}} - B_{0^\circ\text{C.}} = 0.021 \times 10^{-3}$.

If, however, we do the same from the latest Berlin coefficients (given

¹⁾ H. KAMERLINGH ONNES. These Proceedings, 10, 445, 1908. Comm. N^o. 102a.

²⁾ L. HOLBORN und J. OTTO. Zs. f. Phys. 10, 367, 1922, calculated from measurements of: L. HOLBORN und H. SCHULTZE Ann. d. Phys. (4) 47, 1089, 1915.

³⁾ R. WIEBE, V. L. GADDY and C. HEINS. J. Amer. Chem. Soc. 53, 5, 1931.

⁴⁾ L. HOLBORN und J. OTTO. Zs. f. Phys. 38, 365, 1926.

for a series in powers of p) we obtain: J. OTTO ¹⁾: $B_{0^{\circ}\text{C.}} = 0.524^4 \times 10^{-3}$, $B_{100^{\circ}\text{C.}} = 0.5078 \times 10^{-3}$, $B_{100^{\circ}\text{C.}} - B_{0^{\circ}\text{C.}} = 0.017 \times 10^{-3}$ ²⁾.

Hence the comparison with the Berlin values is not conclusive as to the last decimal of $B_{100^{\circ}\text{C.}} - B_{0^{\circ}\text{C.}}$; the agreement of the results obtained by the different experimenters is, however, well within the limit of accuracy mentioned in § 5.

b. In behalf of the comparison of the values of B themselves we add in Table VII, for completing Table VI, the values of B obtained by observers who did not measure both values $B_{0^{\circ}\text{C.}}$ and $B_{100^{\circ}\text{C.}}$.

TABLE VII.

	$B_{0^{\circ}\text{C.}} \times 10^3$	$B_{20^{\circ}\text{C.}} \times 10^3$	$B_{25^{\circ}\text{C.}} \times 10^3$	$B_{100^{\circ}\text{C.}} \times 10^3$
BOKS and KAMERLINGH ONNES ³⁾	0.523	0.512		
HEUSE and OTTO ⁴⁾	0.520			
TANNER and MASSON ⁵⁾			0.515	0.498
KEESOM and VAN SANTEN	0.503	0.499		0.481

As to TANNER and MASSON's values we observe that from a curve representing their results $B_{0^{\circ}\text{C.}} = 0.523 \times 10^{-3}$, $B_{100^{\circ}\text{C.}} = 0.495 \times 10^{-3}$, would follow.

We conclude that the differences between the results obtained by different observers for the absolute values of B are somewhat larger than the mean error we estimated in § 5 for our results.

§ 10. By using our value $B_{100^{\circ}\text{C.}} - B_{0^{\circ}\text{C.}} = -0.0214 \times 10^{-3}$, and KEESOM, BIJL and Miss VAN DER HORST's value (cf. § 7) $a_v^{0-100^{\circ}\text{C.}} = 0.0036609$ for 1 m mercury, we derive

$$a_A = 0.00366130$$

$$T_{0^{\circ}\text{C.}} = 273.127.$$

As, however, still new measurements of the pressure coefficient of helium are going on (cf. § 1), these numbers are still to be considered as preliminary ones.

We gladly record our thanks to phil. nat. docts. H. H. KRAAK for his valuable help at the experiments.

¹⁾ J. OTTO. Zs. f. Instrumentenkunde 48, 257, 1928.

²⁾ Cf. LANDOLT-BÖRNSTEIN, 2er Erg. bd. I, 44.

³⁾ J. D. A. BOKS and H. KAMERLINGH ONNES. Comm. N^o. 170a, The values of B we are calculated by G. P. NIJHOFF. Thesis Leiden 1928, p. 42.

⁴⁾ W. HEUSE und J. OTTO. Zs. f. Instrumentenkunde 49, 267, 1929.

⁵⁾ C. C. TANNER and I. MASSON, Proc. Roy. Soc. (A) 126, 268, 1930.