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Absolute Temperature Scale between 4.2° and 5.2°K†

R. BERMAN* AND C. A. SWENSON
Cryogenic Engineering Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The vapor pressure of helium has been determined between 4.25° and 5.1°K, using a constant volume gas thermometer. An equation is proposed which fits the experimental data closely, and gives temperatures which differ by a maximum of 0.02° from the currently accepted values. The reliability of the value of the boiling point of helium and the thermodynamic consistency of the properties of liquid helium near the boiling point are discussed.

INTRODUCTION

THE currently accepted temperature scale[1] between 4.2° and 5.2°K is largely based on five vapor pressure measurements by Kamerlingh-Onnes and Weber,[2] all above 4.9°. The assumed shape of the vapor pressure curve is not determined solely by these points, but also by the fact that it must join smoothly onto the more accurately known portion of the curve below 4.2°.

It has recently been suggested by Worley, Zemansky, and Boorse[3] that this accepted curve could be in error by as much as 0.06° at 4.8°. They found that an interpolation formula for the resistance of carbon resistors, which fitted vapor pressure data between 1.8° and 4.2° and at the hydrogen triple point, gave temperatures which were lower than the accepted values for helium vapor pressures above one atmosphere, and were in close agreement with values given by an extrapolation of the equation of Keesom and Lignac[4] (which fits the vapor pressure data closely between 2.2° and 4.2°).

We had need for accurate values of dP/dT in this region in order to calculate values of the vapor density from previous experiments.[5] It was noticed that values of dP/dT at 4.3° as calculated from the accurately known portion of the accepted scale and from the formula valid above 4.2° were in disagreement. This suggested that the two curves did not join sufficiently smoothly near the boiling point, where both should apply. Thus doubts were cast on the equation which had been used to fit the data of Kamerlingh-Onnes and Weber.

We have successfully used carbon resistance thermometers for thermal conductivity work between 4° and 80°K, but the discrepancies noticed by Worley *et al.* were not evident since the resistance thermometers were calibrated directly against a gas thermometer over the whole range during the course of each experiment, and an interpolation formula was not required. As our apparatus contained a vapor pressure bulb for calibrating the gas thermometer, it was possible to adapt it for an accurate determination of the helium vapor pressure between 4.2° and 5.2°K.

APPARATUS

Figure 1 is a schematic drawing of the apparatus. The copper gas thermometer (volume roughly 100 cc) is supported on the liquid helium vessel by a length of thin-walled copper-nickel tubing. The heat conduction along this tube is quite small, and the actual cooling of the gas thermometer is achieved by a method similar to that described by Swenson and Stahl.[6] The liquid helium is kept under a slight overpressure by means of

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* On leave from the Clarendon Laboratory, University of Oxford, Oxford, England.

[1] H. van Dijk and D. Schoenberg, Nature **164**, 151 (1949).

[2] H. Kamerlingh-Onnes and Sophus Weber, Leiden Comm. **147b** (1915).

[3] Worley, Zemansky, and Boorse, Phys. Rev. **93**, 45 (1954).

[4] W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 196.

[5] R. Berman and J. Poulter, Phil. Mag. **43**, 1047 (1952).

[6] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. (to be published).

an external bubbler, and by opening the needle valve the gas thermometer can be cooled by liquid helium forced through the copper coil which is silver-soldered to its base. The rate of cooling can be easily controlled by the needle valve, and once a desired temperature is reached, it can be maintained constant through the use of a heater which is attached to the inlet of the copper coil. Changes in temperature are detected rapidly by a carbon resistance thermometer used in conjunction with a Leeds-Northrup Type K potentiometer. The resulting temperature control was such that during the course of a gas thermometer reading (about 20 min), the drift in the vapor pressure of the helium corresponded to less than 0.001°.

The gas thermometer is connected to a 15-mm bore mercury manometer by stainless steel tubing, 0.5-mm inside diameter. The mercury level in the right-hand limb of the manometer is kept constant by adjusting the pressure in the mercury reservoir. The levels are read using a Société Genevoise cathetometer and a 110-cm calibrated Invar scale. The micrometer head of the cathetometer telescope was marked in 0.01-mm intervals, and readings of a mark on the invar scale could be reproduced to a few tenths of a division. However, owing to the greater difficulty of setting on the mercury meniscus, the reproducibility was seldom better than 1 division, or 0.01 mm. This was, for our smallest gas pressure, equivalent to about 0.002°.

The copper vapor pressure bulb (1.5 cc) soldered to the top of the gas thermometer was used initially with nitrogen and hydrogen to calibrate the gas thermometer, and finally to obtain the vapor pressure of liquid helium. It is not necessary to measure the vapor pressures to great accuracy, since in the range with which we were concerned, the vapor pressure changes were about a thousand times greater than the changes in the gas thermometer pressure.

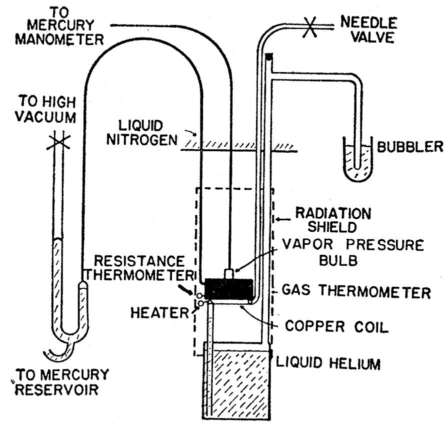

FIG. 1. A schematic drawing of the apparatus. The vacuum jacket and surrounding liquid nitrogen bath are not shown.

REDUCTION OF THE READINGS TO ABSOLUTE TEMPERATURE[7]

An idealized constant volume gas thermometer would consist only of a volume at the temperature to be measured, and of a dead volume in the manometer at room temperature. The ratio of volumes should be as large as possible, and in our case was about 33:1. The pressure-temperature relationship for a gas thermometer is given mainly by two factors, the quantity of gas in the system, and the dead volume ratio. These can be determined by measuring the pressure in the system at two known thermometer temperatures. We chose temperatures near the boiling points of nitrogen and hydrogen, since the vapor pressure-temperature relationships for these substances have been measured accurately by other workers.[8,9]

The system cannot in practice be divided into two such discrete volumes and one must take into account temperature variations of the capillary which connects the two volumes. In our apparatus the major contribution to this effect is due to the gas in the capillary between the liquid nitrogen bath and the gas thermometer. The result is a temperature-dependent addition to the dead volume, which varies from 8 percent when the thermometer is near 80°, to 12 percent at 20°, and 14 percent at 4°K. These figures were calculated, assuming a linear variation with temperature of the thermal conductivity of the stainless steel in the range from 4° to 80°K.[10] The effects of these corrections are quite small, and represent less than 0.001° near 4°.

The system is not truly of constant volume because of the thermal expansion of the copper thermometer. This effect is again small (0.001° near 4°K), and the volume change between 80° and 20°K was taken to be 0.075 percent.[11,12] The deformation of the thermometer due to pressure changes was also checked and found to be less than one or two parts in 10^5, so that it could be neglected.

No corrections were necessary for the changes in the amount of helium adsorbed on the copper surface, since an estimate showed that they were very small.[13] In any event, since data were taken for pressures differing by a factor of four, such effects, if appreciable, would have become evident.

The major reason for taking data at three different filling pressures (giving sensitivities of 0.5, 1, and 2 cm

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[7] For further details see, for example, H. J. Hoge and F. G. Brickwedde, J. Research Natl. Bur. Standards **22**, 351 (1939).

[8] W. H. Keesom and A. Bijl, Physica **4**, 305 (1937).

[9] Keesom, Bijl, and van der Horst, Proc. Koninkl. Akad. Wetenschap. Amsterdam **34**, 1223 (1931).

[10] R. Berman, Phil. Mag. **42**, 642 (1951).

[11] Calculated from Grüneisen's law, assuming cubic expansion of 48×10^{-6} at room temperature and a Debye Θ of 330° for copper. For our purposes the deviation from this law for copper at low temperatures, discussed by Bijl and Pullan (see reference 12), is sufficiently small to be neglected.

[12] D. Bijl and H. Pullan, Phil. Mag. **45**, 290 (1954).

[13] For steel, see H. P. R. Frederikse and C. J. Gorter, Physica **16**, 402 (1950).

Hg/degree) was to test the validity of two rather significant corrections which had to be applied. These were for the nonideality of the helium gas and the thermomolecular effect in the capillary leading from the thermometer. The thermomolecular effect was negligible for the calibration data, but the nonideality was still appreciable even at 80°K.

Typical values for the corrections near 4° were as follows: For the smallest filling of the thermometer, neglecting the nonideality would produce an error of 0.023°, and neglecting thermomolecular effects would produce an error of 0.007° in the opposite direction. For the largest filling, the corresponding figures are 0.104° and 0.0005°. These corrections were calculated from the virial coefficient[14] and thermomolecular data[15] given in Keesom's book.

The hydrostatic head correction for both the height of the liquid and height of the vapor above the liquid in the vapor pressure thermometer was small enough to be neglected.

In two of the cases (fillings of 2 and 4 cm Hg pressure) the quantity of gas in the system was determined by measurements close to the hydrogen boiling point, using the vapor pressure data of Keesom, Bijl, and van der Horst.[9] In the third case no hydrogen point data were taken, and the thermometer filling was determined using the accepted (1948 Cambridge) vapor pressure tables for a point at 4.245°K.

RESULTS

The data from all three runs could be represented by the following equation with a mean deviation of 0.002^5° and a maximum error of 0.007°:

$$\log_{10}p_{\mathrm{cm}} = 0.97864 - (2.77708/T) + 2.5\log_{10}T \quad (1)$$

(where p is measured in cm Hg at 20°C). The constants of this equation were determined by passing a least-squares straight line through a plot of ($\log_{10}p_{\mathrm{cm}} - 2.5\log_{10}T$) *vs* $1/T$.

Figure 2 gives the deviation of our individual experimental points from the above equation. As can be seen, the scatter is independent of thermometer pressure and, hence, confirms the accuracy of our corrections.

The deviations from our equation of the original experimental points and proposed curve of Kamerlingh-Onnes and Weber[2] are also shown. This curve is of importance, since it is used exclusively by Keesom in his book to describe measurements between 4.2° and 5.2°K. The third curve gives the deviations of the accepted scale from our equation. Considering the experimental data on which this curve is based, the agreement is indeed satisfactory. Equation (1) fits smoothly onto the accepted scale at 4.25° and reproduces it fairly well at lower temperatures, with a deviation of 0.01° at 3.5°K. It actually reproduces the accepted scale more faithfully between 4.0° and 4.3° than does the formula of Keesom and Lignac.[4] This latter equation, when extrapolated to temperatures above 4.3°, gives temperatures that are increasingly low, with an error of 0.05° at 4.8°K.

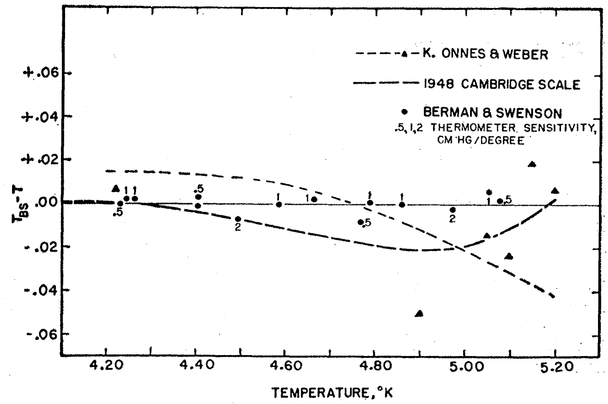

FIG. 2. The deviations of various experimental data and vapor pressure formulas from our proposed scale. T_{BS} is the temperature as given by Eq. (1).

Recent investigations of the absolute temperature scale below 4.2°[16] have assumed the value of the boiling point of helium to be 4.216°. This temperature is the result of three measurements by Keesom and Schmidt[17] based on the boiling point of normal hydrogen (20.381°). When we use the same vapor pressure data for hydrogen,[18] we confirm their helium boiling point to 0.002°. This is true for each of the two runs in which we calibrated the gas thermometer near 20°K. Woolley, Scott, and Brickwedde,[19] however, give a boiling point of hydrogen which is roughly 0.01° higher, and this, if correct, would increase the helium boiling point by 0.002°. The liquid helium temperature scale near 4°K, based on liquid hydrogen data, is therefore subject to this basic uncertainty, which is of the same order as the experimental accuracy of Keesom and Schmidt[17] and of ourselves.

The critical temperature as given by Kamerlingh-Onnes and Weber is roughly in agreement with our data. We did not make a separate determination of the critical point, but have assumed the critical pressure of 171.8 cm Hg (at 0°C) reported by them, and find a temperature of 5.206(±0.003)°K corresponding to this pressure. The critical pressure apparently has not been checked since these original determinations in 1911.[20]

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[14] W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 49.

[15] See reference 14, p. 122.

[16] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954). We are grateful to Dr. Roberts for a preprint of their paper.

[17] W. H. Keesom and G. Schmidt, Physica **4**, 828 (1937).

[18] Since our vapor pressure measurements were taken within an hour after condensing the hydrogen from a cylinder, we have assumed that our hydrogen consisted of the normal mixture.

[19] Woolley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).

[20] H. Kamerlingh-Onnes, Leiden Comm. **124b** (1911).

In Table I are given values of the vapor pressure for temperatures between 4.2 and 5.2°K, calculated according to Eq. (1).

THE LATENT HEAT AND VAPOR DENSITY ABOVE THE NORMAL BOILING POINT

In a previous paper[5] measurements of an apparent latent heat of evaporation, L^*, of helium were described. L^* was defined in terms of the mass of vapor evolved upon heating, ignoring the quantity of vapor which remains in the volume previously occupied by the evaporating liquid. The true latent heat is then given by

$$L = L^*(1-\rho_V/\rho_L), \tag{2}$$

where ρ_V and ρ_L are the vapor and liquid densities, respectively. It was shown that the only directly determined value of this vapor density in the neighborhood of the normal boiling point was not compatible with values derived from the virial coefficients or by the extrapolation of isotherms. It is, however, possible to calculate the vapor density directly from the values of L^* if reliable values of dP/dT are known, since by combining the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T(\rho_V^{-1}-\rho_L^{-1})} \tag{3}$$

with Eq. (2), we obtain

$$\rho_V = (TdP/dT)/L^*. \tag{4}$$

TABLE I. The vapor pressure, vapor and liquid densities, and latent heat of evaporation for saturated helium above 4.2°K.

1 T °K	2 P cm Hg at 20°C	3 ρ_V 10^{-2} g/cc	4 ρ_L g/cc	5 L cal/mole
4.2	75.09	1.69_5	0.1263	19.7_5
4.25	78.74	1.77_5	0.1251	19.4_5
4.3	82.50_5	1.86	0.1238	19.1_5
4.35	86.39	1.95	0.1226	18.8_5
4.4	90.39	2.05	0.1214	18.5
4.45	94.51	2.15	0.1202	18.1
4.5	98.75	2.27	0.1189	17.6
4.55	103.1		0.1177	
4.6	107.6		0.1165	
4.65	112.2		0.1153	
4.7	117.0		0.1142	
4.75	121.8			
4.8	126.8			
4.85	131.9			
4.9	137.2			
4.95	142.6			
5.0	148.1			
5.05	153.8			
5.1	159.6			
5.15	165.6			
5.2	171.6			
5.206	172.5 (Critical pressure for Hg at 20°C)			

We have calculated values of ρ_V from the values of L^*, and the values of dP/dT derived from Eq. (1), and give these in column 3 of Table I. The discrepancy noted previously[5] between calculated vapor densities and the direct measurements of Mathias *et al.*[21] is actually increased by the change in temperature scale. Below 4.2° values calculated in this way are in excellent agreement with values derived from the virial coefficients, as given, for example, by Erickson and Roberts.[16]

In column 4 of Table I are given values of ρ_L found by Kamerlingh-Onnes and Boks,[22] corrected to our proposed temperature scale. Using our values of ρ_V and these values of ρ_L, we have calculated the true latent heat above the normal boiling point. The agreement with the smoothed values given by Keesom[23] is good, although above 4.2°K this is somewhat fortuitous, since the values of both ρ_V and dP/dT used by Keesom differ by several percent, but in opposite directions, from the values we have derived. At 4.0° and 4.2°K our values of latent heat also agree to within 0.5 percent with values calculated from the free energies by Erickson and Roberts.[16]

SUMMARY

These experiments have shown that the currently accepted values of the boiling point and critical point of helium are quite accurate. The deviations from the accepted scale above 4.3°K which were suggested by Worley, Zemansky, and Boorse[3] (0.06°) were confirmed as to sign, but were actually only one-third as great. This would seem to cast doubt on the validity of using an interpolation formula for carbon resistors between 4.2° and the triple point of hydrogen, unless the behavior of the specific resistor has been checked previously against a gas thermometer.

We have also shown that at the boiling point of helium the vapor density, virial coefficients, and vapor pressure curve are in thermodynamic agreement. A further check on the second virial coefficient is given by the fact that our boiling point, obtained with pressures of several centimeters of mercury in the gas thermometer, agrees so precisely with that obtained by Keesom and Schmidt,[17] who used pressures several hundred times less.

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[21] Mathias, Crommelin, Kamerlingh-Onnes, and Swallow, Leiden Comm. **172b** (1925).

[22] H. Kamerlingh-Onnes and J. D. A. Boks, Leiden Comm. **170b** (1924).

[23] See reference 14, p. 231.