THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 96, NO. 3 NOVEMBER 1, 1954

Orthobaric Densities of He^3 1.3°K to 3.2°K*

EUGENE C. KERR
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received July 19, 1954)

Saturated liquid and vapor densities of He^3 have been measured by a direct method in the temperature range of 1.3°K to 3.2°K. The experimental data are represented by an empirical equation to probable errors of 0.1 percent for the liquid phase and of 1.3 percent for the vapor phase.

I. INTRODUCTION

THE only previous measurements of the orthobaric† densities of He^3 are those of Grilly, Hammel, and Sydoriak.[1] They measured directly the difference between the liquid and vapor densities and then derived the component densities by distributing one-half of each measured density difference above and below a derived rectilinear diameter. This mean density line was obtained by drawing a straight line between a low temperature point, at which the vapor density was assumed to be ideal, and a critical density point which was located at the same fractional distance between the calculated Dieterici and van der Waals densities as was the corresponding value for He^4. Their reported uncertainties in terms of liquid density range from 2 percent at 1.27°K to 5 percent at 2.79°K.

The purpose of the present investigation was to measure the liquid and vapor densities directly and independently and in such a way that the above uncertainties in the densities could be reduced by a factor of at least ten.

II. APPARATUS AND MATERIALS

The section of the apparatus external to the cryostat was the same as that used for an earlier investigation on deuterium and tritium.[2] It contained a calibrated constant volume gas pipette of approximately 50-cm^3 capacity for measuring the gas at room temperature, a small Toeppler pump for controlling the transfer of gas to the low-temperature part of the system, and the necessary manometers to determine gas pressures in the various parts of the system.

The gas measuring system was connected to the pycnometer by means of a Monel metal capillary tube, 0.013 inch i.d. This capillary was also connected to a Wallace and Tiernan differential pressure gauge used to read the pressure in the He^3 system. This gauge was used as a null instrument by adjusting the case pressure until the indicating needle was brought to the same scale reading as was used when the gauge volume was calibrated. The case pressure of the gauge was then observed on a mercury manometer.

In order to avoid serious fluctuations in the amount of gas contained in the capillary tube where it passed through severe temperature gradients, it was vacuum jacketed from a point one inch above the lid of the helium bath Dewar to a point just above the density bulb. In addition, 30 cm of the 33 cm jacketed length was plated rather heavily with copper to insure nearly uniform temperature throughout this length. With one end of this section immersed in liquid nitrogen, which completely covered the helium bath Dewar, and the other end in the helium bath, it was estimated that the temperature gradient in the plated section was 0.1°K/cm, whereas in the 3-cm unplated portion the gradient was 24°K/cm. This arrangement minimized *variations* in the amount of gas in the dead space from run to run. The additional conductivity of the copper plating vaporized about 4 cm^3 of bath helium per hour.

The Pyrex glass bulbs for liquid or vapor densities were attached to the Monel metal capillary by means of a small Kovar metal to Pyrex glass joint. A butt-

---

* This paper is based on work performed under University of California contract with the U. S. Atomic Energy Commission.

† Orthobaric density: the density of a liquid when in equilibrium with its own vapor, or of a vapor in equilibrium with its own liquid phase, at a specified temperature.

[1] Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949).

[2] Eugene C. Kerr, J. Am. Chem. Soc. **74**, 824 (1952).

joint and sleeve arrangement was used between the Monel capillary and the Kovar metal tube so that the separate sections could be calibrated independently and then assembled without change in volume at the joint. The bulb used for liquid density measurements had a neck drawn down to a fine capillary (3.93×10^{-4} cm^3/mm) on which a calibration line was etched and filled. It was calibrated to this mark and also between the mark and the tip of the Kovar tubing by weighing it empty and when filled with mercury. The volume obtained was corrected to He bath temperatures by use of the extrapolated expansion data of Buffington and Latimer.[3] It was further checked in place by filling it with He^4 at 4.0°K using the same techniques as for the He^3 density measurements. The volume obtained with He^4 was 0.07 percent higher than that obtained by the mercury weighing with expansion correction. Using 0.1298 g/cm^3 for the density of He^4 at 3.955°K, the average of six measurements gave 0.11148 ± 0.00006 cm^3 for the volume of this bulb.

A larger bulb (0.7465 ± 0.0003 cm^3) was used for the vapor density measurements in order to minimize the ratio of dead space volume to bulb volume for these smaller densities.

The helium bath temperature was controlled by an electrical heater balanced against the pumping rate on the bath by means of the signal generated in a carbon resistance thermometer in one arm of a bridge circuit. This bath control system has been described by Sommers.[4] The temperatures are observed, in terms of the vapor pressure of the bath helium, on mercury or on butyl sebacate manometers.

Liquid density measurements were made by transferring known amounts of gas, measured in the calibrated pipette, to the small density bulb until the liquid meniscus was brought close to the etched mark on the neck of the bulb. The distance between the meniscus and the mark was measured with a small cathetometer. If several measurements were to be made in the same series, the temperature was then lowered, an additional small amount of gas was added to bring the meniscus back to the vicinity of the mark, and the measurement was repeated. With each measurement, the bath pressure and the He^3 pressure were recorded. After completion of all of the liquid density measurements, the apparatus was disassembled and the density bulb was sealed off at the etched calibration mark. After reassembly, the amount of gas required to fill the dead space with dew point pressure gas was measured as a function of bath temperature.

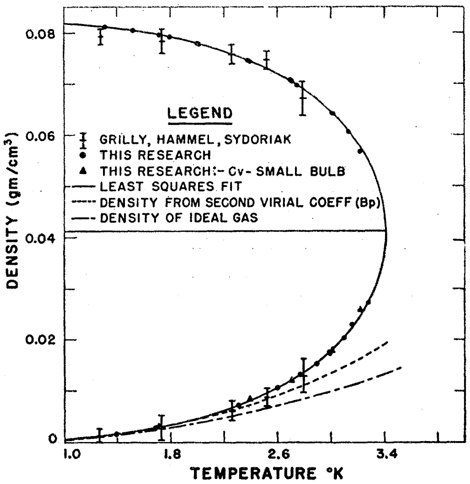

FIG. 1. Orthobaric densities of He^3.

Vapor densities were obtained from the measurement of isotherms of the number of moles of He^3 required to fill the density bulb (plus dead space) as a function of the He^3 pressure. Extrapolation of each isotherm to the saturation pressure gave the number of moles of gas required to fill the system at saturation. Five to six points were obtained on each isotherm, most of them being at pressures above 0.75 of the saturation pressure, so that extrapolation could be made unambiguously. Calibration of the dead space was made subsequently in the same manner as was used for the liquid density dead space measurements.

The purity of the He^3 used was determined by analysis with a Consolidated Nier type isotope ratio mass spectrometer. The only detectable impurities were 0.28 percent He^4 and 0.02 percent nitrogen. The atomic weight of He^3 was taken as 3.0162 on the chemical scale.[5]

All observed manometer readings, except those of the helium bath, were corrected to mm of Hg at 0°C and standard acceleration of gravity. The helium bath manometer readings were corrected to 20°C in order to coincide with the "agreed" temperature scale for He^4 vapor pressures.[6] Temperatures so obtained were corrected to the Kistemaker temperature scale T_K[7] by use of the smoothed data given by Abraham, Osborne, and Weinstock.[8]

The saturation pressures of He^3 used for dead space corrections and for extrapolation of the vapor density isotherms were obtained from the helium bath temperature and the data on He^3 vapor pressures given by Abraham, Osborne, and Weinstock.[8] Observed vapor pressures read from the null Wallace and Tiernan gauge and backing manometer agreed with the calculated pressures to within 0.5 mm on the average.

III. EXPERIMENTAL RESULTS

The results of fifteen measurements of the density of saturated liquid He^3 in the temperature range 1.30°K

---

[3] R. M. Buffington and W. M. Latimer, J. Am. Chem. Soc. **48**, 2305 (1926).

[4] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

[5] J. Mattauch and A. Flammerfeld, "Isotopic Report," Z. Naturforsch. (1949).

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

[7] J. Kistemaker, Physica **12**, 272, 281 (1946).

[8] Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950).

TABLE I. He³: Orthobaric liquid densities.

T_K °K	Density (obs) g/cm³	Density (calc) g/cm³	Deviation (%)
1.304	0.08121	0.08121	0.00
1.516	0.08051	0.08053	+0.02
1.709	0.07964	0.07971	+0.09
1.787	0.07935	0.07931	−0.05
1.998	0.07803	0.07803	0.00
2.013	0.07792	0.07792	0.00
2.378	0.07470	0.07472	+0.03
2.393	0.07444	0.07456	+0.16
2.698	0.07072	0.07054	−0.26
2.710	0.07040	0.07035	−0.07
2.748	0.06971	0.06973	+0.03
3.010	0.06434	0.06437	+0.05
3.020	0.06423	0.06412	−0.17
3.135	0.06067	0.06086	+0.31
3.223	0.05681	0.05775	+1.62

to 3.22°K are given in Table I. Here, the first column is the temperature in degrees Kelvin on the Kistemaker scale, the second is the liquid density in g/cm³, the third is the liquid density calculated from Eq. (4) below, and the fourth is the deviation in percent between the observed and calculated values.

The results of twelve measurements of the orthobaric vapor density are given in Table II in which the columns have the same significance as in Table I.

Several attempts were made to fit the data into equations related to modified van der Waals equations such as those given by Haggenmacher,[9] in which the molar volume is expressed as a function of (T/P) and of the critical constants. Within any reasonable assignment of the critical constants, these equations did not give results consistent with the precision of the experimental data. Consequently, a completely empirical method, based on the symmetry properties of the density *vs* temperature curves, was adopted.

The density of either of the co-existing phases can be represented by the identity

$$\rho=\tfrac{1}{2}(\rho_L+\rho_v)\pm\tfrac{1}{2}(\rho_L-\rho_v). \tag{1}$$

In this case, the first term on the right, which represents the mean·density or rectilinear diameter, can be expressed with sufficient precision:

$$\rho_m=0.04117_3+4.14\times10^{-5}T. \tag{2}$$

The remaining portion of Eq. (1) can best be represented by

$$\tfrac{1}{2}(\rho_L-\rho_v)=(A_0{}^2+YT^2)^{\frac{1}{2}}. \tag{3}$$

The variable Y was fitted to several simple polynomial expansions in T, the best of which was a linear form. Thus the vapor and liquid densities can be represented by:

$$\rho=A_0+BT\pm(A_0{}^2+CT^2+DT^3)^{\frac{1}{2}}, \tag{4}$$

where $A_0=0.04117_3$, $B=4.14\times10^{-5}$, $C=-3.3015\times10^{-6}$, and $D=-4.1876\times10^{-5}$.

Densities obtained from Eq. (4) are shown in Tables I and II as ρ_{calc}. The deviations between the observed and calculated densities give for the probable error of a single measurement: 0.00006 g/cm³ or 0.09 percent for the liquid phase measurements and 0.00016 g/cm³ or 1.13 percent for the vapor phase measurements.

The liquid density point at 3.223°K was not included in the equation fitting since preliminary least squares solutions showed that the deviation of this point was more than five times the probable error. However, an examination of Fig. 1 will show that, had only the liquid density data been considered, the best curve could well have come much closer to the plotted points at 3.135°K and 3.223°K. Such a fit would also have had an apex nearer the accepted critical temperature of 33.35 ±0.02°K than that given by Eq. (4) of 3.416°K.

Extrapolation by means of Eq. (4) gives the liquid density at 0°K as 0.08235 g/cm³ which is almost equal to twice the critical density of 0.04131 g/cm³. This is the only case, within the author's knowledge where such a relationship occurs.

Liquid and vapor densities according to this equation are shown by the solid curve in Fig. 1 on which are superimposed the observed densities and the densities as given by Grilly, Hammel, and Sydoriak.[1] Included as triangles along the vapor density curve are five points obtained by the use of the small liquid density bulb. Because of the relatively greater uncertainty in the dead space corrections for these measurements, as compared to those obtained with the larger bulb, these points were not included in Table II nor in the least squares summations.

The dashed curves in the figure represent the vapor densities as calculated from the perfect gas law and those calculated from the pressure expansion form of the virial equation of state in closed form involving only the second virial coefficient. Densities derived from the virial equation in the inverse volume expansion, actually give a much better fit with respect to the experimental data below 2.6°K than do those obtained from the pressure expansion. However, in the closed

TABLE II. He³: Orthobaric vapor densities.

T_K °K	Density (obs) g/cm³	Density (calc) g/cm³	Deviation (%)
1.395	0.00146	0.00152	+3.94
1.689	0.00269	0.00268	−0.37
2.305	0.00713	0.00706	−0.99
2.596	0.01059	0.01051	−0.76
2.767	0.01315	0.01317	+0.15
2.890	0.01529	0.01550	+1.35
2.991	0.01756	0.01776	+1.13
2.994	0.01774	0.01783	+0.50
3.097	0.02030	0.02058	+1.36
3.157	0.02293	0.02247	−2.04
3.160	0.02297	0.02257	−1.77
3.282	0.02727	0.02752	+0.91

---

[9] John E. Haggenmacher, J. Am. Chem. Soc. **68**, 1123–26 (1946).

form used, the inverse volume form gives imaginary densities above about 2.8°K. This indicates that, when the data are available, the vapor densities will most probably be best represented by the inverse volume virial equation with at least the third virial coefficient included.

The values used for the second virial coefficient in the calculations were obtained from the calculations of Kilpatrick, Keller, Hammel, and Metropolis.[10]

Since Eq. (4) is somewhat cumbersome to use, the densities have been evaluated at even temperatures (Kistemaker scale) and are given in Table III. If estimated contributions of possible systematic errors are combined with the precision indices given above, the results in this table should be reliable to about 0.3 percent for the liquid phase up to 3.1°K and to about 2 percent for the vapor phase between 1.6°K and 3.1°K. At low vapor densities, it appears that the nature of Eq. (4) and the method of evaluation of its constants tend to give values which are too high and that vapor densities calculated from the second virial coefficients (in $1/v$ form) will give more reliable values below about 1.6°K. The present experimental method does not have enough inherent accuracy at low densities to decide this point.

TABLE III. Calculated liquid and vapor densities at even temperatures.

T_K °K	Liquid density g/cm^3	Vapor density g/cm^3	ΔH_{vap} cal/mole
1.0	0.08185	0.00058	9.10
1.2	0.08147	0.00098	9.76
1.4	0.08093	0.00154	10.32
1.6	0.08020	0.00228	10.71
1.8	0.07924	0.00325	11.02
2.0	0.07801	0.00450	11.15
2.2	0.07645	0.00608	11.05
2.4	0.07448	0.00806	10.71
2.6	0.07200	0.01056	10.11
2.8	0.06882	0.01376	9.19
3.0	0.06462	0.01798	7.88
3.1	0.06193	0.02067	7.01
3.2	0.05861	0.02400	5.91
3.3	0.05416	0.02845	3.36

The last column of Table III gives the heat of vaporization in calories per mole as calculated from the thermodynamic relation

$$\Delta H_{\text{vap}} = T(V_{\text{gas}} - V_{\text{liq}})dP/dT. \tag{5}$$

The molal volume of the gas was obtained from the gas densities given in the third column of the table at temperatures of 2.0°K and above. Below 1.2°K molar volumes given by the density virial equation were used. In the intervening region, a graphical interpolation between the densities given by Eq. (4) and those given by the density virial equation was used. Since the two curves agree to within 0.00030 g/cm^3 over most of this region, little uncertainty is introduced by this method. Values of dP/dT were obtained from the vapor pressure data of Abraham, Osborne, and Weinstock.[8]

---

[10] Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).