

DENSITY MEASUREMENTS
OF HELIUM AND HYDROGEN AT
LOW TEMPERATURES

19 JUN 1963

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ZAKARIA EL HAG ALI EL HADI

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INSTITUUT LORENTZ
voor theoretische natuurkunde
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AT LOW TEMPERATURES

ZAKARIYA EL HAG ALI EL HADI

PROFESOR DE EL MATEMATICA (DUTCH) IN 1968

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DENSITY MEASUREMENTS OF HELIUM AND HYDROGEN AT LOW TEMPERATURES

PROEFSCHRIFT

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DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE
RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE
RECTOR MAGNIFICUS DR P. MUNTENDAM, HOOGLERAAR
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1968

KONINKLIJKE DRUKKERIJ VAN DE GARDE N.V.
ZALTBOMMEL (NEDERLAND)

DENSITY MEASUREMENTS
OF HELIUM AND HYDROGEN AT
LOW TEMPERATURES

PROEFSCHRIFT

TER VERVOLGING VAN DE GRAAD VAN DOCTOR IN
DE WISSENSCHAPPEN MET HET BEWIS VAN DE
BUREAUKRANTING VAN DE WISSENSCHAPPEN VAN DE
RECHTEN VAN DE WISSENSCHAPPEN VAN DE
IN DE WISSENSCHAPPEN VAN DE WISSENSCHAPPEN
VAN DE WISSENSCHAPPEN VAN DE WISSENSCHAPPEN
VAN DE WISSENSCHAPPEN VAN DE WISSENSCHAPPEN

Promotor: Prof. Dr C. J. GORTER

Dit proefschrift is bewerkt onder toezicht van

Dr M. DURIEUX

ZAKARIA DE HAG ALLE HADI

VERBODEN TOEGANG TOT DE WISSENSCHAPPEN

1921
KONINKLIJKE DRUKKERIJ VAN DE WISSENSCHAPPEN
VAN DE WISSENSCHAPPEN VAN DE WISSENSCHAPPEN

STELLINGEN

I

De in dit proefschrift gevonden waarden voor de derde viriaalcoëfficiënt van waterstofgas verschillen van die welke door Ter Harmsel zijn gebruikt voor de berekening van de temperatuurafhankelijkheid van de dampdruk (p - T relatie) van vloeibare waterstof. De invloed van deze verschillen op de berekende waarden van dp/dT bij temperaturen beneden 21°K is kleiner dan 0,2%.

Ter Harmsel, H., Proefschrift, Leiden (1966).

II

Er zijn ernstige bezwaren aan te voeren tegen de waarden van de tweede viriaalcoëfficiënt van gasvormig ^4He die bepaald zijn uit recente metingen van de geluidssnelheid bij lage temperaturen en die aanzienlijk hoger zijn dan de uit gasdichtheidsmetingen afgeleide waarden.

Plumb, H. H. en Cataland, G., *Metrologia* **2** (1966) 127 en persoonlijke mededeling.

Grimsrud, D. T. en Werntz, J. H., *Phys. Rev.* **157** (1967) 181.

III

De opmerking van Joiner dat het door Cladis voorgestelde verband tussen stroom en spanning voor supergeleiders van de tweede soort in een loodrecht magneetveld niet in overeenstemming is met de huidige inzichten over de processen die optreden bij de fluxbeweging is onjuist.

Joiner, W. C. H., *Phys. Rev. Letters* **19** (1967) 895.

Cladis, P. E., *Phys. Rev. Letters* **19** (1967) 116.

IV

De kwaliteit van een platina-weerstandsthermometer voor het meten van lage temperaturen kan beter worden beoordeeld aan de hand van de constantheid van de weerstand bij $4,2^\circ\text{K}$ dan van die van de weerstand bij 0°C .

V

Bij metingen van de soortelijke warmte met een nauwkeurigheid die beter is dan 0,1% zouden de kleine oneffenheden welke voorkomen in de T_{58} -temperatuurschaal hinderlijk kunnen zijn.

VI

De door Newhouse aangegeven temperatuurafhankelijkheid van het thermodynamische kritische veld H_c voor onzuiver niobium is niet consistent met die voor zuiver niobium.

Newhouse, V. L., Applied Superconductivity (John Wiley and Sons, Inc., New York, 1964) p. 5.
Ferreira da Silva, J., Proefschrift, Leiden (1967).

VII

Het verdient aanbeveling het warmtegeleidings-mechanisme van drukkontakten nader te bestuderen teneinde een warmteschakelaar te kunnen ontwerpen voor gebruik beneden 1°K.

VIII

Het is gewenst dat instellingen zoals het Bureau International des Poids et Mesures in hun officiële publikaties steeds grootheden-vergelijkingen gebruiken.

IX

Het zou voorkeur verdienen de internationale praktische temperatuurschaal tussen 14 and 20°K primair te definiëren met behulp van de waterstof-dampspanningsthermometer in plaats van met platinathermometers en enkele vaste punten.

X

Voor de economische groei van Soedan is uitbreiding van de bestaande voedsel-verwerkende industrie belangrijker dan vergroting van de katoenproductie.

XI

Het geluk van een mens is in sterkere mate afhankelijk van het verkrijgen van geestelijke evenwichtigheid dan van het verkrijgen van inzicht in natuurverschijnselen.

ERRATA

The pressures in the first column of table I, chapter I (p. 10) are given with an accuracy higher than can be warranted. A very slightly modified table is given in *Physica* (1968) and in the Communications from the Kamerlingh Onnes Laboratory of the University of Leiden, No. 364a.

On p. 25, 4th line, replace 2% by 1.5%.

On p. 41, ref. 7, replace *Cryogenics* 2 (1961) 81 by *J. Res. Nat. Bur. Stand.* 68A (1964) 121.

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المجلد الثاني - كتاب في تاريخ الدولة العثمانية

تأليف
د. محمد علي

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The contents of this thesis will be published in *Physica* in 1968, and in the *Communications from the Kamerlingh Onnes Laboratory of the University of Leiden*, No. 364.

CHAPTER I

THE DENSITY OF LIQUID ^4He UNDER ITS SATURATED VAPOUR PRESSURE

Synopsis

The density of liquid ^4He under a pressure slightly higher than its saturated vapour pressure has been measured pycnometrically between 1.2 and 5.1°K. The available data of the isothermal compressibility have been used to calculate the density along the saturation curve. The results are presented in tabular form and are compared with data from other sources.

1. *Introduction.* Many experiments¹⁻¹³) have been made to determine the density of liquid helium under its saturated vapour pressure. The earlier measurements were made to obtain general information on the density-temperature relation. Later on, emphasis was laid on the exact behaviour of the density-temperature curve near the λ -point^{4) 5)}. In recent years attention was focussed on the determination of the density as a function of the temperature near the critical point^{9) 10) 13)}.

Measurements of the density of liquid helium can be made by a direct method using a calibrated pycnometer which is filled with liquid. The amount of helium gas liberated from the pycnometer on warming is measured at room temperature. This experiment can be carried out in two ways. One can determine the volume of the liquid by observing the liquid level in a short glass capillary connected to the calibrated pycnometer. In this way the density can be measured under the saturated vapour pressure and it is also possible to determine the expansion coefficient of the liquid directly by watching the liquid level as the temperature changes. The other possibility is to fill the pycnometer through a fine metal capillary to a pressure slightly higher than the saturated vapour pressure. Since the volume of the capillary can be made small compared to the volume of the pycnometer, an approximate knowledge of the liquid level in the capillary is sufficient. Data of the isothermal compressibility of the liquid are required to correct the experimental results for the small overpressure.

A somewhat less direct method of determining the density of the liquid

under the saturated vapour pressure is based on the extrapolation of high pressure p - V - T data of the liquid^{6) 7)}.

Densities can also be obtained by an indirect method which involves the measurement of the refractive index⁸⁻¹⁰⁾ or the dielectric constant¹¹⁻¹³⁾ of the liquid. The refractive index n is related to the density ρ by the Lorenz-Lorentz law

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3M) \rho N_A \alpha \quad (1)$$

where M is the molar mass and $N_A \alpha$ is the molar polarizability. The dielectric constant ϵ and the density ρ are related through the Clausius-Mossotti equation

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3M) \rho N_A \alpha. \quad (2)$$

These methods are credited with the ease of operation at many closely spaced temperatures in one run in a temperature range where the density changes rapidly with temperature, *e.g.*, near the critical point. In addition, they permit the determination of the density of a very thin layer of liquid, unlike the direct methods which only allow the determination of the average density over the height of the pycnometer. This is of importance for measurements close to the critical temperature. These methods also avoid the tedious processes of calibrations, gas-metering and dead space corrections which are inherent in the direct methods. However, the results have to be normalized at a known density to determine the molar polarizability. Moreover, one has to assume that the molar polarizability is constant and that the Lorenz-Lorentz law or the Clausius-Mossotti relation is strictly obeyed.

A complete review of the measurements of the density of liquid helium under its saturated vapour pressure below 4.2°K was given by Kerr and Taylor⁴⁾ in 1964. Direct methods for the determination of the liquid density were used by Kamerlingh Onnes and Boks¹⁾, Mathias, Crommelin, Kamerlingh Onnes and Swallow²⁾, Kerr³⁾ and Kerr and Taylor⁴⁾. Atkins and Edwards⁵⁾ determined the expansion coefficient of liquid helium along the saturation curve below the λ -point. Keesom and Keesom⁶⁾ and Edeskuty and Sherman⁷⁾ obtained liquid densities at the saturation pressure from extrapolation of high pressure p - V - T data. Edwards⁸⁾ measured the refractive index of liquid helium over the temperature range 1.6-4.2°K. These measurements were extended up to 5.16°K by Edwards and Woodbury⁹⁾. Recently Edwards¹⁰⁾ reported liquid densities from refractive index measurements at temperatures very close to the critical point. The densities of the liquid were derived from measurements of the dielectric constant by Grebenkemper and Hagen¹¹⁾, Chase, Maxwell and Millett¹²⁾ and Roach and Douglass¹³⁾.

Some of the direct measurements were not performed under optimum conditions. For example, Kerr's pycnometer³⁾ was considerably smaller than the optimum size which might be used for the accurate determination

of liquid ^4He densities. The lack of means to determine with sufficient accuracy the amount of gas in the dead space above the liquid level in the glass capillary connected to the pycnometer was one of the reasons that Kerr and Taylor⁴⁾ did not extend their measurements to temperatures higher than 2.8°K .

The following remarks are based upon a review of the available data on the density of liquid ^4He under saturation pressure.

a. Apart from the two density values reported by Mathias *e.a.*²⁾ no direct measurements have been made at temperatures above 4.4°K .

b. Small but systematic differences exist between the densities reported by Kerr and Taylor⁴⁾ and those derived by Edwards⁸⁾ from his refractive index measurements.

c. There is a slight discrepancy of the order of 0.07 of a per cent between the densities measured by Kerr and Taylor⁴⁾ with a pycnometer and those deduced using the integration of the expansion coefficient of the liquid as measured by Atkins and Edwards⁵⁾ at temperatures between 1.2°K and the λ -point.

The above considerations made the present research desirable. It incorporates the results of direct density measurements at 21 different temperatures between 1.2 and 5.1°K .

2. *Experimental equipment.* The apparatus consists of a calibrated copper pycnometer which can be filled with liquid helium through a fine stainless steel capillary to a pressure slightly higher than the saturated vapour pressure. The temperature of the pycnometer is measured with a germanium thermometer while the temperature gradient along the filling capillary is determined by thermocouples. The equipment includes a manometer system

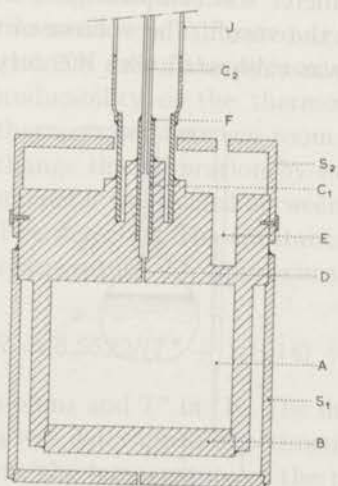


Fig. 1. The pycnometer.

which is used to measure the pressure in the pycnometer and a gas-metering system.

a. The pycnometer. The pycnometer reservoir *A* (see fig. 1) was made of copper in the form of a thick-walled hollow cylinder machined from a solid drawn bar. The end plate *B* was soft-soldered to the cylinder. A stainless steel capillary *C*₁ had been previously hard-soldered to the reservoir. The bore *D* was 0.5 mm in diameter. Capillary *C*₁ was 60 mm in length and had an inner diameter of 0.7 mm. A cavity *E* in which a capsule-type germanium thermometer could be placed was drilled in the cylinder.

The volume of the pycnometer (up to *F*, see fig. 1) was (17.1148 ± 0.0010) cm³ at 0°C. This value was the average obtained from six sets of calibrations with air-free distilled water. The density of air-free water with natural content of D₂O under a pressure of one standard atmosphere and at 0°C was taken as 0.999840 g/cm³^(14, 15).

The calibration assembly is sketched in fig. 2. The principle of the method is to distill air-free water from a detachable glass flask *G* into the pycnometer *H*, after the careful removal of air from the entire assembly. The level of the water can be seen in a calibrated glass capillary *C* connected to *C*₁. Flask *G* is connected to *C* by narrow glass tubing. The difference in weight of the flask before and after the distillation process gives the amount of liquid transferred to the pycnometer, provided that the glass tubing and the stopcocks are free from condensed water vapour. The process can be reversed by distilling water from the pycnometer into *G*. A check that no air is entrapped can be made by admitting air into *C* when the pycnometer is filled with water and observing the change in the level of the water in *C*. In absence of entrapped air bubbles the level drops only through a small distance because the water in the pycnometer is compressed. After the calibration of the pycnometer was completed, *C*₁ was cut at a point about 15 mm above the top of the vessel. The volume of the removed part, up to a reference mark on *C*, was calibrated with mercury.

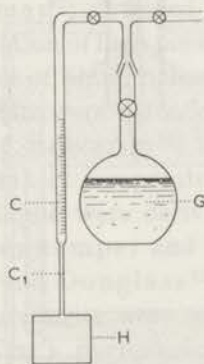


Fig. 2. Calibration assembly for the pycnometer.

The volume contraction of the pycnometer between 273°C and 5°K was computed using the coefficient of thermal expansion of copper¹⁶⁻²⁴). It was found that $v_{5^{\circ}\text{K}}/v_{273^{\circ}\text{K}} = 0.99112$, where v is the volume of the vessel. The change in volume of the pycnometer at liquid helium temperatures is negligible.

The fine stainless steel capillary C_2 (450 mm long, 0.3 mm in bore) was joined to capillary C_1 . This fine capillary was not extended over the whole length of the cryostat since the pycnometer was evacuated through it before the beginning of the measurements. C_2 was joined to another stainless steel capillary C_3 (500 mm long, 0.7 mm in bore). C_3 was extended by a stainless steel capillary C_4 (400 mm long, 1.0 mm in bore) to connect the pycnometer to the manometer and gas-metering systems. All capillaries were previously calibrated with mercury. The capillaries were surrounded by a glass tube J which could be evacuated or filled with helium exchange gas. A spiral was made in the upper part of C_3 to prevent tension when the apparatus is cooled. The pycnometer was surrounded by two copper shields, S_1 and S_2 , one at the bottom and one at the top (see fig. 1). Both shields were open to the helium bath which was contained in a helium dewar 100 cm in depth. A heater with a resistance of 40 Ω was placed in the bath about 40 mm below the pycnometer.

b. The germanium thermometer. A capsule-type germanium thermometer, made by Bell Telephone Laboratories and supplied to us by Professor H. A. Boorse of Columbia University, New York, was placed in the cavity E . A thin film of vacuum grease was used to improve the thermal contact between the pycnometer and the thermometer. The resistance of the thermometer was measured with a potentiometer using a constant voltage (2.1 mV) over the thermometer. Thermal e.m.f.'s were eliminated in the usual way by reversing the current.

The germanium thermometer was calibrated against the vapour pressure of ^4He between 1.2 and 5.2°K using the pycnometer as a vapour pressure thermometer. The reproducibility of the thermometer was checked. Repeated cycling of the thermometer between room temperature and helium temperatures did not change the calibration by more than 2×10^{-3} °K in 3 years. When the thermometer was cycled between 5.2 and 1.2°K no change in the calibration could be detected. The resistance R of the thermometer could be related to a temperature T^* , approximately equal to T_{58} ²⁵), by the equation

$${}^{10}\log R = 8.5522/(T^* + 1.1014) + 0.4808 \quad (3)$$

where R is expressed in ohms and T^* in °K. The difference between T^* and T_{58} as a function of T_{58} was determined experimentally. This difference did not exceed 0.01°K. Thus, the temperature of the pycnometer could be determined by the above interpolation formula together with a graph of

$(T^* - T_{58})$ versus T_{58} for any measured resistance between 1.2 and 5.2°K.

In practice, the thermometer was calibrated at the beginning of every measurement against the ^4He vapour pressure in order to be independent of any possible resistance shift of the thermometer on thermal cycling between room temperature and helium temperatures. Normally, the thermometer was calibrated at a desired temperature T_1 . But at the time that the pycnometer was completely filled with liquid helium, the temperature of the pycnometer would usually be a few millidegrees different from T_1 due to a small temperature drift of the bath. This small temperature change could easily be calculated from the change in the resistance of the thermometer and dR/dT obtained from the previous calibrations.

c. The thermocouples. The temperature along the stainless steel capillaries leading to the pycnometer reservoir were determined at 10 points with gold + 0.03 per cent (at.) iron versus chromel thermocouples²⁶). Insulated gold-iron wires of 0.08 mm in diameter and insulated chromel wires of 0.09 mm in diameter were obtained from Johnson Matthey and Co. Ltd., London. These thermocouples have a sensitivity higher than $10 \mu\text{V}/^\circ\text{K}$ throughout the temperature range 1–300°K.

A single length of gold-iron wire was, by means of small copper plates, thermally anchored to but electrically insulated from the capillaries at 10 points. Chromel wires were soldered to the copper plates at these points. All these wires were led outside the cryostat and were connected to copper wires at 0°C. The thermocouples were calibrated at 77°K, between 24 and 14°K, and at helium temperatures.

d. The manometers and the gas-metering system. These are shown schematically in fig. 3. Vapour pressures less than 45 mm Hg were measured with an oil manometer. Vapour pressures in the range 45–1500 mm Hg were measured with a mercury manometer K . The vacuum side of K was either connected to the high vacuum pump for the measurement of pressures less than 800 mm Hg or opened to the atmosphere for the measurement of higher pressures. This manometer was placed in an aluminium box with perspex windows to reduce temperature gradients along the manometer. The heights of the mercury levels were measured with a Precision Tool Company cathetometer on an invar scale. Corrections due to capillary depression, inhomogeneity of the temperature of the mercury and errors in the calibration and the expansion coefficient of the invar scale were discussed by Ter Harme¹²⁷) who had built a large part of the manometer and gas-metering systems for the measurement of the heat of vaporization of hydrogen and helium. Vapour pressures higher than 1500 mm Hg were measured with a long mercury manometer L placed in an aluminium U-beam. This manometer was closed at one end and had a scale on the glass wall. The scale was calibrated against an invar scale. An oil differential manometer M was used to measure differences between the pressures over the bath and in the pycnometer.

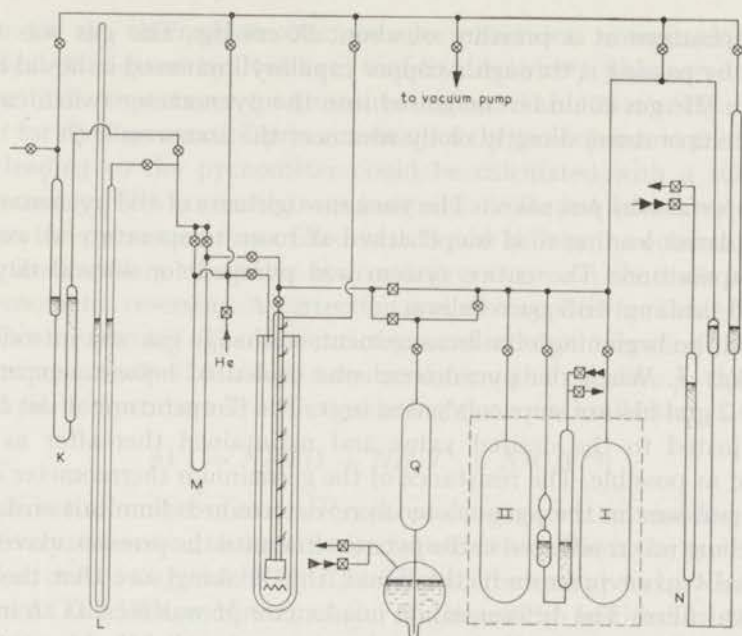


Fig. 3. Schematic drawing of experimental apparatus.

The gas liberated from the pycnometer on warming it to room temperature was measured in the thermostated vessels I and II. The volumes of these vessels, as determined by Ter Harmsel, were

$$V_{\text{I}} = (8232.2 \pm 0.2 + (t - 20) 0.091 + (p - 760) 0.001) \text{ cm}^3$$

and

$$V_{\text{II}} = (8779.3 \pm 0.2 + (t - 20) 0.097 + (p - 760) 0.001) \text{ cm}^3$$

where p is the pressure in the vessels expressed in mm Hg at 0°C and t is the temperature of the vessels in $^\circ\text{C}$. The vessels were placed in a thermostat which maintained the temperature constant to within $\pm 0.01^\circ\text{C}$ or better. The temperature t was measured with an accuracy of 0.01°C with a mercury-in-glass thermometer which was calibrated against a standard platinum resistance thermometer. The pressure of the gas collected in the vessels was always higher than 400 mm Hg and was measured with the constant volume manometer N which was described in detail in ref. 27. The volume of the glass tubing connecting the vessels I and II with the pycnometer and the constant volume manometer was $(183.1 \pm 0.3) \text{ cm}^3$ and was determined by gas pressure measurements using a calibrated vessel of approximately the same volume placed in the thermostat. The temperature of these glass tubes was measured at different places with an accuracy of 0.1°C .

e. Purification of ^4He . Helium gas obtained from a high pressure cylinder was held in contact with activated charcoal cooled to liquid nitro-

gen temperature at a pressure of about 90 cm Hg. The gas was further purified by passing it through a copper capillary immersed in liquid helium. The pure ^4He gas could be condensed into the pycnometer (when cooled to helium temperature) directly or by means of the compressor Q .

3. *Experimental procedure.* The vacuum-tightness of the pycnometer and the capillaries leading to it was checked at room temperature as well as at low temperatures. The entire system was pumped for several days with repeated flushing with pure helium.

Before the beginning of a measurement, exchange gas was introduced in the jacket J . When the pycnometer was cooled to helium temperatures, about 0.2 g of helium were condensed in it. The temperature of the cryostat was adjusted to the desired value and maintained thereafter as nearly constant as possible. The resistance of the germanium thermometer and the vapour pressure in the pycnometer were determined simultaneously. Then more helium was condensed in the pycnometer until the pressure exceeded the saturated vapour pressure of the liquid, thus making sure that the pycnometer was filled. The differential oil manometer M was used as an indicator to adjust the pressure in the pycnometer to a value slightly in excess of the saturation pressure. When the pressure in the pycnometer became constant, measurements of the resistance of the germanium thermometer and the pressure in the pycnometer were made simultaneously. The pycnometer was thereupon isolated from the manometers K , L and M , connected to the evacuated gas-metering system and slowly warmed to room temperature. The gas was collected in vessels I and II.

For the calculation of the density it was necessary to know the position of the liquid helium level in the capillary when the pycnometer was filled with liquid. It was assumed that the liquid level in the capillary was at the same height as the liquid level in the helium bath because the temperature at the liquid level in the capillary as derived from the measured pressure was only a few millidegrees higher than the bath temperature. The thermocouple readings indicated that the temperature of the capillary below the bath level (which was always kept below the junction of C_2 to C_3) was almost equal to the bath temperature. It was estimated that the position of the liquid level in the fine capillary C_2 could be determined in this way within ± 2 cm. An uncertainty of 2 cm in the liquid level means an uncertainty of only 0.008% in the volume of the liquid.

4. *Data reduction.* a. Reduction of measured pressures. The measured pressures were reduced to mm Hg at 0°C and standard gravity (1 mm Hg at 0°C and standard gravity = 133.322 N/m^2). Corrections were applied for the thermomolecular pressure effect, the "aerostatic" pressure head and the hydrostatic pressure head whenever appropriate. The cor-

rection for the thermomolecular pressure effect was computed from the numerical data given by Roberts and Sydoriak²⁸). This correction was of very little importance for pressures higher than 100 mm Hg. The correction for the "aerostatic" pressure head of the gas column in the capillary tubes leading to the pycnometer could be calculated with a sufficiently high accuracy. This correction was insignificant for low pressures.

When the pycnometer was filled with liquid helium the column of liquid in the fine capillary exerted a hydrostatic pressure on the bulk helium in the pycnometer reservoir. A correction was also applied for this effect.

b. Gas-metering. The amount of gas collected on warming the pycnometer to room temperature was calculated from the pressure p , the volume V^* and the temperature T of the gas using the equation of state

$$pV^* = NRT(1 + NB/V^* + N^2C/V^{*2}) \quad (4)$$

where N is the number of moles, R is the molar gas constant and B and C are, respectively, the second and third virial coefficients. The molar gas constant was taken as 8.3143 J/mol °K²⁹). The virial coefficients given by Keesom³⁰) were used. The IBM computer of the Mathematical Institute of the State University of Leiden was programmed to compute N by an iterative method.

A correction was applied for the amount of gas in the capillaries which was present above the meniscus of the liquid helium. This correction could be calculated accurately since the temperatures along the capillaries were measured with thermocouples. The uncertainty in the amount of gas present in this dead space was estimated to be about 3%, giving rise to an uncertainty in the liquid density of about 0.003% at 5.1°K and less than 5×10^{-6} % at 1.2°K.

c. The density under the saturated vapour pressure. The density ρ^L of liquid ⁴He under a pressure p very slightly in excess of the saturation pressure is given by $\rho^L = N'M/v$, where v is the volume of the liquid ⁴He in the reservoir of the pycnometer and the fine capillary, N' is the number of moles of liquid ⁴He and M is the molar mass of ⁴He ($M = 4.0026$ g/mol on the ¹²C-basis³¹)).

The corresponding density ρ_s^L under the saturated vapour pressure has been calculated using the available data of the isothermal compressibility $k_T = (1/\rho)(\partial\rho/\partial p)_T$.

The isothermal compressibility data reported by Edwards and Woodbury³²) and others⁵⁾¹²⁾³⁰) have been used. Edwards and Woodbury claim an accuracy of 3% in k_T for temperatures below 4.2°K. Above 4.2°K the uncertainty in k_T increases and may amount up to 15% at 5.0°K. For the purpose of the present research no stringent requirement on the accuracy of k_T is demanded since for most of the experimental points the correction on the measured density is less than 0.05%. At low temperatures and particularly in the helium II region the influence of this correction be-

comes very small. At higher temperatures, especially above 4.5°K, the data for k_T are scarce and uncertain. The available data on the equations of state of the liquid and the gas have been analyzed to derive a smooth and consistent set of values for $(\partial\rho/\partial p)_T$.

It is estimated that the error introduced by this correction is less than 0.001% below the λ -point, but gradually increases to about 0.02% at 4.2°K and that it can reach 0.2% at 5.1°K.

5. *Experimental results.* The results of 21 independent measurements of the density of liquid ^4He between 1.2 and 5.1°K are listed in table I. Here the first column gives the pressure p at which the density ρ^L (second column) is measured. The saturated vapour pressure p_s (at the temperature

TABLE I

Measured densities ρ^L of liquid ^4He under a pressure p slightly higher than the saturation pressure p_s . ρ_s^L are the densities under saturation pressure. $\Delta\rho_s^L = \rho_s^L - (\rho_s^L)_{sm}$ where $(\rho_s^L)_{sm}$ are the smoothed values of ρ_s^L .							
p mm Hg, 0°C	ρ^L g/cm ³	p_s mm Hg, 0°C	T_{58} °K	ρ_s^L g/cm ³	$p - p_s$ mm Hg, 0°C	$10^3 \frac{\rho^L - \rho_s^L}{\rho_s^L}$	$10^3 \frac{\Delta\rho_s^L}{(\rho_s^L)_{sm}}$
5.831	0.145179	0.7536	1.2270	0.145167	5.077	0.08	-0.12
7.429	0.145268	4.385	1.5418	0.145261	3.044	0.05	+0.09
20.250	0.145494	14.691	1.8474	0.145480	5.559	0.09	+0.01
34.456	0.145824	28.620	2.0654	0.145809	5.836	0.10	-0.10
55.019	0.146103	41.072	2.2062	0.146065	13.947	0.26	-0.19
74.542	0.145056	69.178	2.4431	0.145040	5.364	0.11	+0.01
125.983	0.143190	119.808	2.7381	0.143171	6.175	0.14	-0.00
174.037	0.141546	168.828	2.9501	0.141528	5.209	0.13	+0.01
252.643	0.139155	246.054	3.2114	0.139129	6.589	0.19	-0.00
339.633	0.136514	335.133	3.4507	0.136494	4.500	0.15	-0.16
456.514	0.133358	449.153	3.7009	0.133319	7.361	0.29	-0.17
459.719	0.133303	453.175	3.7089	0.133269	6.544	0.26	+0.24
592.37	0.129669	586.81	3.9513	0.129632	5.56	0.29	-0.08
773.64	0.125181	757.86	4.2120	0.125041	15.78	1.12	+0.09
787.72	0.124849	772.14	4.2319	0.124710	15.58	1.11	+0.59
907.77	0.120883	903.39	4.4039	0.120834	4.39	0.41	-0.97
1084.25	0.116118	1071.75	4.6008	0.115923	12.50	1.68	+0.13
1267.06	0.110193	1253.98	4.7909	0.109870	13.08	2.94	+0.80
1381.64	0.105188	1376.39	4.9079	0.105001	5.25	1.78	+0.11
1492.72	0.100055	1487.20	5.0076	0.099734	5.52	3.22	-0.31
1609.6	0.093098	1605.1	5.1080	0.092472	4.5	6.77	+3.7

at which ρ^L is measured) and the corresponding temperature according to the T_{58} -scale are given, respectively, in the third and fourth columns. The density ρ_s^L of liquid ^4He under the saturated vapour pressure is listed in the fifth column and it is obtained by applying a correction to the measured density ρ^L to account for the small overpressure, $p - p_s$, given in the sixth column. The data in the seventh column are intended to give an impression of the magnitude of the correction for the slight overpressure. The last

column gives the deviation of ρ_s^L from the smoothed density $(\rho_s^L)_{sm}$ discussed in section 7.

It can be seen from the last column that the deviations of the experimental results from the smooth values are of the order of 0.01% below the λ -point, mostly less than 0.02% below the boiling point and not exceeding 0.1% between 4.2 and 5.0°K.

6. *Comparison with other data.* In fig. 4 the results for ρ_s^L between 1.2 and 4.2°K are compared with the data calculated from a table given by Kerr and Taylor⁴) and designated here by $(\rho_s^L)_{KT}$. This table gives smoothed values of the molar volume V_s^L of liquid ⁴He under saturation pressure. Below 2.3°K the table is based on graphical and analytical smoothing and above 2.3°K it has been calculated from the equation

$$(V_s^L)_{KT} = (27.1040 + 0.0067224 p_s - 1.692 \times 10^{-746/p_s}) \text{ cm}^3/\text{mol} \quad (5)$$

where p_s is expressed in mm Hg at 0°C.

From $(V_s^L)_{KT}$ the densities $(\rho_s^L)_{KT}$ were calculated using the relation

$$(\rho_s^L)_{KT} = 4.0026 \text{ g mol}^{-1}/(V_s^L)_{KT}. \quad (6)$$

Data from other sources, corrected to T_{58} whenever applicable, are also included in fig. 4.

It can be seen from fig. 4 that below the λ -point the results of the present research deviate slightly from the data of Kerr and Taylor. They agree almost exactly with the densities obtained from the integration of the expansion coefficient data of liquid ⁴He along the saturation curve given by Atkins and Edwards⁵), normalized to the density $\rho_s^L = 0.145183 \text{ g/cm}^3$ at 1.2°K. It should be noted that the total variation of the density between 1.2 and 2.0°K is only 0.35 per cent.

The densities derived by Edwards⁸) from his measurements of the refractive index were recalculated using for the molar polarizability the value 0.12427 cm³/mol. This value, which is slightly lower than the value 0.12454 cm³/mol used by Edwards, was chosen by Kerr and Taylor. It can be seen that the results of the present research agree closely with the recalculated results of Edwards. In particular, the shape of the density *versus* temperature curve obtained from Edwards' data between 3 and 4.2°K is confirmed by the present results. Above 4.2°K deviations from eq. (5) become significant, *e.g.*, at 4.5, 4.8 and 5.1°K these deviations are about 1%, 4% and 14%, respectively.

It is interesting to note that the earliest measurements of the liquid density made by Kamerlingh Onnes and Boks¹) do not show any significant deviations from the present results. The small deviations that do occur can adequately be explained by their explicitly-mentioned uncertainty in the temperature of the tank used for metering the collected gas.

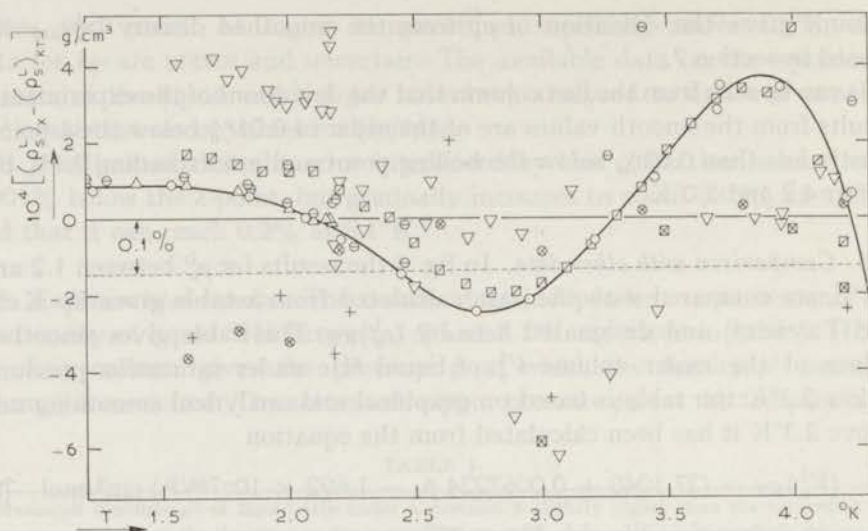


Fig. 4. Densities $(\rho_s^L)_x$ of liquid ^4He under saturation pressure from different sources compared with $(\rho_s^L)_{KT}$ calculated from the table of Kerr and Taylor below 2.3°K and from eqs. (5) and (6) above 2.3°K .

- | | | |
|---|---------------------------|----------------------------------------------------------------|
| ○ | This research | (pycnometric method) |
| ⊙ | Kamerlingh Onnes and Boks | (pycnometric method) |
| ▽ | Kerr | (pycnometric method) |
| △ | Atkins and Edwards | (integrated expansion coefficient) |
| ⊠ | Edwards | (refractive index, $N_A z = 0.12427 \text{ cm}^3/\text{mol}$) |
| + | Grebenkemper and Hagen | (dielectric constant) |
| ⊞ | Keesom and Miss Keesom | (extrapolation of high pressure p - V - T data) |
| ⊗ | Edeskuty and Sherman | (extrapolation of high pressure p - V - T data) |

Between 4.2 and 5.1°K the density ρ_s^L of the liquid under the saturation pressure p_s could be approximated by the equation

$$(\rho_s^L)_{\text{approx}} = F_1(T) + A_0(p_c - p_s)^\alpha + B_0(p_c - p_s)^\gamma \quad (7)$$

where

$$F_1(T) = (0.06969 - 0.001555(T - 5)) \text{ g/cm}^3 \quad (T \text{ in } ^\circ\text{K})$$

$$A_0 = 0.00420513 \text{ g cm}^{-3} \text{ mm Hg}^{-\alpha}$$

$$\alpha = 0.361$$

$$B_0 = 3.47 \times 10^{-7} \text{ g cm}^{-3} \text{ mm Hg}^{-\gamma}$$

$$\gamma = 1.37$$

and p_c is the critical pressure, taken equal to 1705.0 mm Hg at 0°C^{13} .

In this way $(\rho_s^L)_{\text{approx}}$ is given as the sum of the term $F_1(T)$, which approximately represents the rectilinear diameter, and two terms which vanish at the critical pressure. This method of representation of ρ_s^L is analogous to that used by Kerr³³) for the orthobaric densities of ^3He . A discussion of eq. (7) is given in chapter II. At present it should be emphasized that the

equation for $(\rho_s^L)_{\text{approx}}$ is an empirical relation which is used here to compare the results of the present research with data from other sources and to obtain smoothed values of the density.

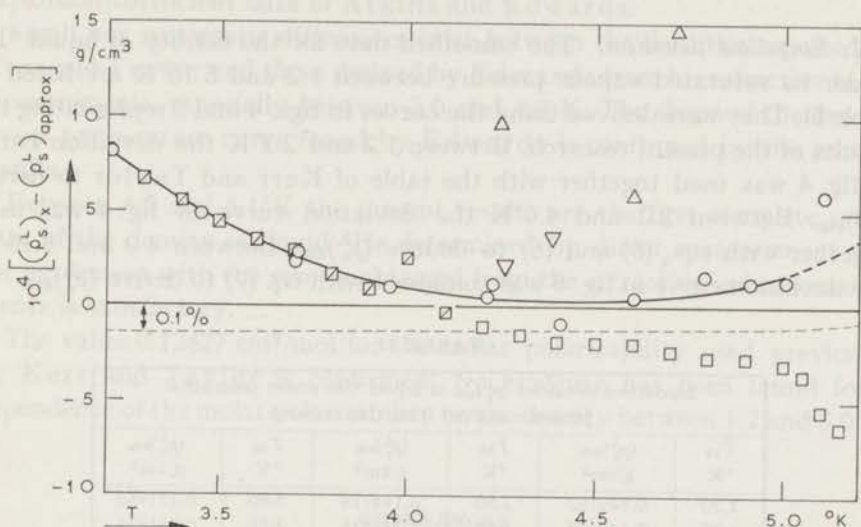


Fig. 5. Densities $(\rho_s^L)_x$ of liquid ^4He under saturation pressure from different sources compared with $(\rho_s^L)_{\text{approx}}$ defined by eq. (7).

- This research (pycnometric method)
- △ Mathias *e.a.* (pycnometric method)
- ▽ Kerr (pycnometric method)
- ▧ Edwards (refractive index, $N_{A\alpha} = 0.12427 \text{ cm}^3/\text{mol}$)
- Edwards and Woodbury (refractive index, $N_{A\alpha} = 0.12427 \text{ cm}^3/\text{mol}$)

The differences $(\rho_s^L)_x - (\rho_s^L)_{\text{approx}}$ are given in fig. 5 for the various data of the density of liquid ^4He under its saturated vapour pressure. As was mentioned before, the results of Edwards⁸) and Edwards and Woodbury⁹) have been recalculated using for the molar polarizability the value $0.12427 \text{ cm}^3/\text{mol}$. Moreover, all temperatures have been reduced to T_{58} whenever applicable. It can be seen that the results of the present research differ slightly and up to 0.5 per cent at 5.0°K from the recalculated results of Edwards and Woodbury. A possible explanation of the difference could be that the temperature of the cell in which the refractive index was measured by Edwards and Woodbury was slightly higher than the temperature in the bath where the temperature was measured. On the other hand, it is possible that the difference is due to a variation of the molar polarizability with density or to a deviation from the Lorenz-Lorentz law. The differences between the present results and the three density values determined by Mathias *e.a.*²) lie within the accuracy with which the temperature of their pycnometer and the amount of the collected gas were measured.

The recent data of the density of liquid ^4He under saturation pressure very close to the critical temperature reported by Edwards¹⁰⁾ and Roach and Douglass¹³⁾ will be discussed in chapter II.

7. *Smoothed densities.* The smoothed data for the density of liquid ^4He under its saturated vapour pressure between 1.2 and 5.15°K are listed in table II. They were derived using the curves in figs. 4 and 5 representing the results of the present research. Between 1.2 and 2.3°K the deviation curve in fig. 4 was used together with the table of Kerr and Taylor to derive $(\rho_s^L)_{sm}$. Between 2.3 and 4.0°K the deviation curve in fig. 4 was used together with eqs. (5) and (6) to deduce $(\rho_s^L)_{sm}$. Between 4.0 and 5.15°K the deviation curve in fig. 5 was combined with eq. (7) to derive $(\rho_s^L)_{sm}$.

TABLE II

Smoothed densities $(\rho_s^L)_{sm}$ of liquid ^4He under saturation pressure derived from this research					
T_{sat} °K	$(\rho_s^L)_{sm}$ g/cm ³	T_{sat} °K	$(\rho_s^L)_{sm}$ g/cm ³	T_{sat} °K	$(\rho_s^L)_{sm}$ g/cm ³
1.20	0.145183	2.50	0.144716	3.80	0.131955
1.25	0.145185	2.55	0.144418	3.85	0.131216
1.30	0.145189	2.60	0.144106	3.90	0.130454
1.35	0.145195	2.65	0.143780	3.95	0.129666
1.40	0.145204	2.70	0.143439	4.00	0.128849
1.45	0.145216	2.75	0.143085	4.05	0.128002
1.50	0.145232	2.80	0.142717	4.10	0.127124
1.55	0.145252	2.85	0.142335	4.15	0.126212
1.60	0.145277	2.90	0.141939	4.20	0.125262
1.65	0.145306	2.95	0.141528	4.25	0.124274
1.70	0.145340	3.00	0.141102	4.30	0.123244
1.75	0.145380	3.05	0.140660	4.35	0.122168
1.80	0.145427	3.10	0.140204	4.40	0.121042
1.85	0.145481	3.15	0.139732	4.45	0.119860
1.90	0.145543	3.20	0.139243	4.50	0.118618
1.95	0.145613	3.25	0.138735	4.55	0.117312
2.00	0.145693	3.30	0.138208	4.60	0.115931
2.05	0.145786	3.35	0.137663	4.65	0.114467
2.10	0.145898	3.40	0.137102	4.70	0.112909
2.15	0.146035	3.45	0.136524	4.75	0.111242
2.20	0.146105	3.50	0.135927	4.80	0.109445
2.25	0.145961	3.55	0.135312	4.85	0.107492
2.30	0.145767	3.60	0.134680	4.90	0.105349
2.35	0.145527	3.65	0.134029	4.95	0.102956
2.40	0.145271	3.70	0.133359	5.00	0.100222
2.45	0.145000	3.75	0.132668	5.05	0.096988
				5.10	0.092909
				5.15	0.086926

8. *Conclusion.* The present results of the density of liquid ^4He are estimated to be accurate within 0.05% between 1.2 and 4.2°K and within 0.1% between 4.2 and 5.0°K. Above 5.0°K the accuracy becomes less.

Apart from small deviations, the results of the present research are in good agreement with the data given by Kerr and Taylor below 4.2°K. They agree almost exactly with values obtained from the integration of the expansion coefficient data of Atkins and Edwards.

Small but systematic differences exist between the densities reported by Kerr and Taylor and those derived by Edwards from his refractive index measurements, especially between 3.0 and 4.2°K. The shape of the density *versus* temperature curve found by Edwards is confirmed by the present results.

Between 4.2 and 5.1°K the present results are the first complete set of data of the density of liquid ⁴He determined by direct measurement and the agreement with the results obtained from the refractive index measurements is satisfactory.

The value 0.12427 cm³/mol for the molar polarizability used previously by Kerr and Taylor is confirmed. No evidence has been found for a dependence of the molar polarizability on the density between 1.2 and 5.0°K.

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CHAPTER II

THE DENSITY OF THE SATURATED VAPOUR OF ^4He

Synopsis

The density of ^4He gas at pressures close to saturation has been measured by a direct method over the temperature range from 2.0 to 5.1°K. From the experimental data the density of the saturated vapour has been calculated using the isothermal compressibility of the gas. The data are tabulated and compared with the results of previous measurements and calculations. The behaviour of the rectilinear diameter of ^4He is discussed, taking into account the results for the density of the saturated vapour given here and the results for the density of the liquid under saturation pressure reported in chapter I. An attempt has been made to extrapolate the rectilinear diameter to the critical temperature. The critical density is found to be 0.06976 g/cm³.

1. *Introduction.* In chapter I measurements of the density of liquid ^4He under its saturated vapour pressure have been reported. In this chapter the results of measurements of the density of the saturated vapour will be given.

The determination of the density of the saturated vapour of ^4He has received less attention than the determination of the liquid density. The vapour density has, of course, no anomaly at the λ -point and the density *versus* temperature curve below the λ -point for the vapour is not of as much interest as that for the liquid. However, precise data for the vapour density are of importance in several respects.

Firstly, data for the density of the saturated vapour can be used to obtain information about the virial coefficients in the equation of state

$$pV^G = RT(1 + B/V^G + C/V^{G^2} + \dots) \quad (1)$$

where p is the pressure, V^G the molar volume of the gas, R the molar gas constant, T the temperature and B and C are the second and third virial coefficients, respectively.

Secondly, the knowledge of the density of the saturated vapour as a function of temperature near the critical point is of importance for the study of the critical phenomenon.

Thirdly, the vapour density is related to the molar heat of vaporization L and the vapour pressure-temperature relation through Clapeyron's equation $d\phi_s/dT = L/T(V_s^G - V_s^L)$, where V_s^G is the molar volume of the saturated vapour and V_s^L is the molar volume of the liquid under saturation pressure. $V_s^G = M/\rho_s^G$, where M is the molar mass and ρ_s^G is the density of the saturated vapour. In most cases, not L itself, but the so-called apparent heat of vaporization L_a is measured. L_a is defined as the amount of heat necessary to liberate one mole of helium gas from a calorimeter containing liquid helium. The relation between L_a and L is $L = L_a(1 - V_s^L/V_s^G)$. Substituting this in Clapeyron's equation, one obtains

$$d\phi_s/dT = L_a/TV_s^G. \quad (2)$$

Eq. (2) can be used to calculate a vapour pressure-temperature relation when L_a , ρ_s^G and a reference temperature have been determined accurately. The vapour pressure-temperature relation is, of course, of importance as a means for temperature measurements.

The density of the saturated vapour of ^4He may be determined by pycnometric methods or derived from the measurements of related quantities such as the refractive index and the dielectric constant. The density may also be calculated from the equation of state of the gas or from eq. (2).

Except for three early measurements of the density at 4.2, 4.6 and 4.7°K made by Mathias, Crommelin, Kamerlingh Onnes and Swallow¹⁾, no results of direct measurements of the density of the saturated vapour were ever reported.

In several experiments²⁾³⁾⁴⁾⁵⁾ the densities of helium gas at pressures considerably lower than the saturation pressure have been measured along an isotherm to determine the virial coefficients and the thermodynamic temperature. It is generally assumed that the equation of state with two virial coefficients, B and C , can be used to describe the isotherms up to the saturated vapour pressure at temperatures below 4°K. Higher virial coefficients may be required above 4°K.

Measurements of the refractive index of the saturated vapour of ^4He were carried out by Edwards⁶⁾ from 1.5 to 4.2°K and by Edwards and Woodbury⁷⁾ in the temperature range from 4.2 to 5.1°K. These measurements were extended by Edwards⁸⁾ to temperatures very close to the critical point. These authors derived from their results the density of the saturated vapour using the Lorenz-Lorentz equation. Recently Roach and Douglass⁹⁾ measured the dielectric constant of the saturated vapour at temperatures very near the critical point and used the Clausius-Mossotti relation to calculate the vapour density. The merits of these methods for determining the density from measurements of the refractive index or of the dielectric constant and the assumptions which have to be made to calculate the density were discussed in chapter I.

Calculations of the density of the saturated vapour from eq. (2) using the apparent heat of vaporization and the vapour pressure-temperature relation have been made by Berman and Mate¹⁰⁾ and by Ter Harmsel *e.a.*¹¹⁾ in the temperature range from 2.2 to 5.0°K.

The differences between the data for the density of the saturated vapour derived in different ways are of the order of 0.7 per cent below 4.2°K and they tend to increase at higher temperatures. Therefore it was considered worthwhile to try to determine the vapour density by a direct method. Measurements were made at 23 temperatures between 2.0 and 5.1°K at pressures slightly less than the saturation pressure. From the experimental data the density of the saturated vapour was calculated using the isothermal compressibility of the gas.

2. *Experimental equipment.* Apart from minor modifications, the apparatus was the same as that used for the measurement of the density of liquid ⁴He (see chapter I). The gas-metering system was extended with four small glass bulbs of nominal volumes 5, 15, 50 and 300 cm³, the volumes being calibrated with mercury. They were connected to the constant volume manometer *U*, to the capillary manometer *W* and to the pycnometer *H* by glass capillaries 1.2 mm in bore (see fig. 1). The dead volume in this part of

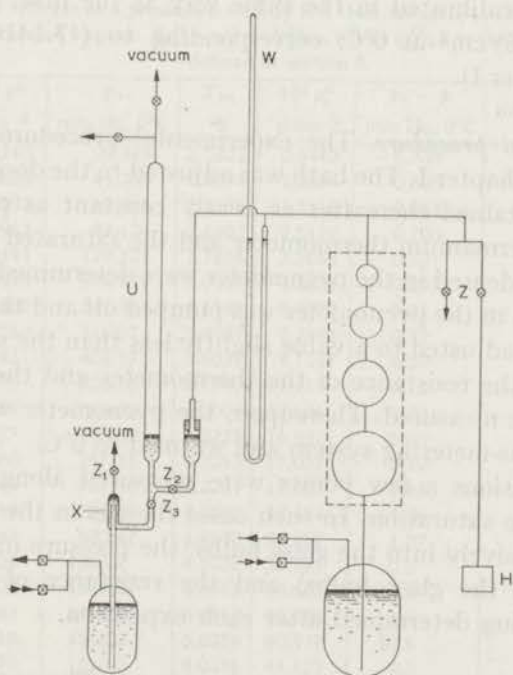


Fig. 1. Equipment for measuring small amounts of gas.

the system was about 8 cm³ and was determined by gas pressure measurements using the small bulbs. The manipulation of the constant volume manometer was facilitated by the capillary manometer on which an approximate value of the pressure was read. The capillary of the capillary manometer had been calibrated with mercury at several places in order to calculate the changes in the dead volume caused by variations of the mercury level. Stopcock *Z* connects the system to the manometers and the gas-metering equipment shown in fig. 3, chapter I. The four bulbs were placed in a thermostated bath and were used for the measurement of amounts of gas which would give too low pressures when expanded into the eight-liter vessel I. They were also used for the measurements of a few points close to saturation along an isotherm.

The constant volume manometer was about 100 cm long and could be used up to pressures of 170 cm Hg by admitting atmospheric pressure to the vacuum side. The mercury was fed into this manometer through an air-trap *X*. *Z*₁, *Z*₂ and *Z*₃ were greaseless glass stopcocks with neoprene diaphragms. Most of the experimental data on the vapour density were obtained using the pycnometer constructed for the measurements of the liquid density. However, a few measurements were made with a second copper pycnometer similar to the first. To reduce gas occlusion at the wall of the pycnometer, care was taken to keep the inner surface smooth and clean. This second pycnometer was calibrated in the same way as the first. Its volume was (17.2950 ± 0.0008) cm³ at 0°C, corresponding to (17.1414 ± 0.0025) cm³ at 5°K (see chapter I).

3. *Experimental procedure.* The experimental procedure was similar to that outlined in chapter I. The bath was adjusted to the desired temperature which was maintained thereafter as nearly constant as possible. The resistance of the germanium thermometer and the saturated vapour pressure of liquid ⁴He condensed in the pycnometer were determined. Following this, the liquid helium in the pycnometer was pumped off and the pressure in the pycnometer was adjusted to a value slightly less than the saturated vapour pressure. Then, the resistance of the thermometer and the pressure in the pycnometer were measured. Thereupon, the pycnometer was connected to the evacuated gas-metering system and warmed to 0°C.

On some occasions a few points were measured along an isotherm at pressures close to saturation. In such cases the gas in the pycnometer was expanded successively into the glass bulbs, the pressure in the system (the pycnometer and the glass bulbs) and the resistance of the germanium thermometer being determined after each expansion.

4. *Data reduction.* a) *Pressure reduction.* The measured pressures were reduced to mm Hg at 0°C and standard gravity. Corrections were made

for the thermomolecular pressure effect and the "aerostatic" pressure head in the same way as was described in chapter I.

b) The temperature. The temperature was essentially derived from the saturated vapour pressure determined at the beginning of each measurement. The germanium thermometer was used to calculate the changes of the temperature of the pycnometer caused by a small temperature drift of the bath during the measurements (see chapter I).

c) The density of the saturated vapour. The density of the ^4He gas under the measured pressure, slightly less than the saturated vapour pressure, was obtained from the experimental results in the way described in chapter I. The corresponding density of the saturated vapour was calculated using values for the isothermal compressibility of helium gas selected from the available data on ^4He isotherms. The uncertainty which is introduced by the compressibility correction is estimated to be less than 0.03 per cent below 4.2°K, but it has a tendency to increase at higher temperatures.

5. *Experimental results.* The results of the measurements are given in table I. The first column gives the pressure p at which the density ρ^G

TABLE I

The density ρ^G of ^4He gas at a pressure p slightly less than the saturation pressure p_s . ρ_s^G is the density of the saturated vapour. $\Delta\rho_s^G = \rho_s^G - (\rho_s^G)_{sm}$ where $(\rho_s^G)_{sm}$ is the smoothed value of ρ_s^G defined in section 8.

p mm Hg, 0°C	$10^3 \rho^G$ g cm ⁻³	p_s mm Hg, 0°C	T_{58} °K	$10^3 \rho_s^G$ g cm ⁻³	$p_s - p$ mm Hg, 0°C	$10^3 \frac{\rho_s^G - \rho^G}{\rho_s^G}$	$10^3 \frac{\Delta\rho_s^G}{(\rho_s^G)_{sm}}$
24.610	0.8190	25.348	2.0222	0.8443	0.738	30.0	+1.5
40.855	1.2638	41.360	2.2091	1.2804	0.505	13.0	+1.3
62.099	1.8002	62.468	2.3936	1.8118	0.369	6.4	-0.4
91.424	2.4963	92.124	2.5907	2.5177	0.700	8.5	-0.8
128.800	3.3499	129.321	2.7834	3.3653	0.521	4.6	+0.5
183.986	4.5548	184.279	3.0081	4.5634	0.293	1.9	+0.5
241.61	5.7887	241.92	3.1989	5.7977	0.31	1.6	+2.7
314.28	7.2762	315.07	3.4009	7.2993	0.79	3.2	-1.0
401.78	9.093	402.17	3.6037	9.1047	0.39	1.3	-1.2
500.01	11.155	500.13	3.7990	11.159	0.12	0.3	-0.5
616.60	13.679	616.80	4.0004	13.686	0.20	0.5	+1.6
759.72	16.777	765.52	4.2227	16.987	5.80	12.3	-0.9
765.19	16.960	767.31	4.2252	17.037	2.12	4.5	-0.3
767.33	17.046	767.96	4.2261	17.068	0.63	1.3	+0.4
784.10	17.417	785.36	4.2501	17.464	1.26	2.7	+0.2
979.40	22.241	980.47	4.4970	22.287	1.07	2.1	+0.0
1265.9	30.709	1266.7	4.8035	30.761	0.8	1.7	-2.0
1366.8	34.402	1369.2	4.9012	34.603	2.4	5.8	-0.1
1489.5	39.963	1491.3	5.0112	40.193	1.8	5.7	+1.6
1497.7	39.518	1508.2	5.0259	40.979	10.5	35.7	-1.2
1507.7	40.778	1510.2	5.0276	41.123	2.5	8.4	-0.4
1510.6	41.028	1511.9	5.0291	41.219	1.3	4.6	-0.4
1597.4	46.604	1598.7	5.1027	46.958	1.3	7.6	+1.3

(second column) is measured. In the third and fourth columns, the saturated vapour pressure and the corresponding temperature according to the T_{58} -scale¹²⁾ are given. The saturated vapour density ρ_s^G obtained from ρ^G by applying the correction for the pressure difference, $p_s - p$, is given in the fifth column. In the seventh column, the magnitude of the compressibility correction is given. The last column gives the deviations of ρ_s^G from the smoothed densities $(\rho_s^G)_{sm}$ defined in section 8.

The three points at 4.22°K were measured together in one run, also the three points at 5.03°K; all other points were measured separately.

6. *Comparison with other data.* The present results for the density of the saturated vapour have been compared with the directly measured saturated vapour densities reported by Mathias *et al.*¹⁾ and with those derived by Edwards⁶⁾ and Edwards and Woodbury⁷⁾ from their measurements of the refractive index as well as with those calculated from the equation of state and with the results obtained by Ter Harmsel *et al.*¹¹⁾ from their data for the apparent heat of vaporization.

The calculations of the saturated vapour density from the equation of state, $p_s V_s^G = RT(1 + B/V_s^G + C/V_s^{G2})$, have been made with two different sets of virial coefficients, the temperature being taken according to the T_{58} -scale. One set of virial coefficients is given by

$$B = (0.6824 - 17.244/T) 22.427 \text{ cm}^3/\text{mol} \quad (3)$$

and

$$C = (5 \times 10^3/T - 4.86 \times 10^6/T^6) \text{ cm}^6/\text{mol}^2 \quad (4)$$

as obtained from an analysis of p - V - T data made by Van Dijk and Ter Harmsel¹³⁾. Eq. (3) was given earlier by Keesom¹⁴⁾ for the temperature range from 5 to 60°K but later Kistemaker¹⁵⁾ found that it could be used down to 1.8°K. For the second set of virial coefficients the B -values given by Kilpatrick, Keller and Hammel¹⁶⁾ have been used, together with the C -values resulting from an analysis performed by Clement¹⁷⁾:

$$C = (1500/\sqrt{T} - 7.5 \times 10^6/T^7) \text{ cm}^6/\text{mol}^2. \quad (5)$$

The differences between the data from various sources are shown in figs. 2 and 3. (For measurements prior to 1958, the temperatures were reduced to the T_{58} -scale).

In fig. 2 the saturated vapour density $(\rho_s^G)_{eq}$ calculated from the equation of state using T_{58} and the set of virial coefficients given by eqs. (3) and (4) was used as a reference up to 4.5°K. At higher temperatures the deviations of ρ_s^G from $(\rho_s^G)_{eq}$ can be as large as 6% at 4.7°K. For vapour pressures higher than 1200 mm Hg ($T_{58} > 4.7^\circ\text{K}$) the equation of state does not even give a real value for the density at saturation when the values of B and C mentioned above are used.

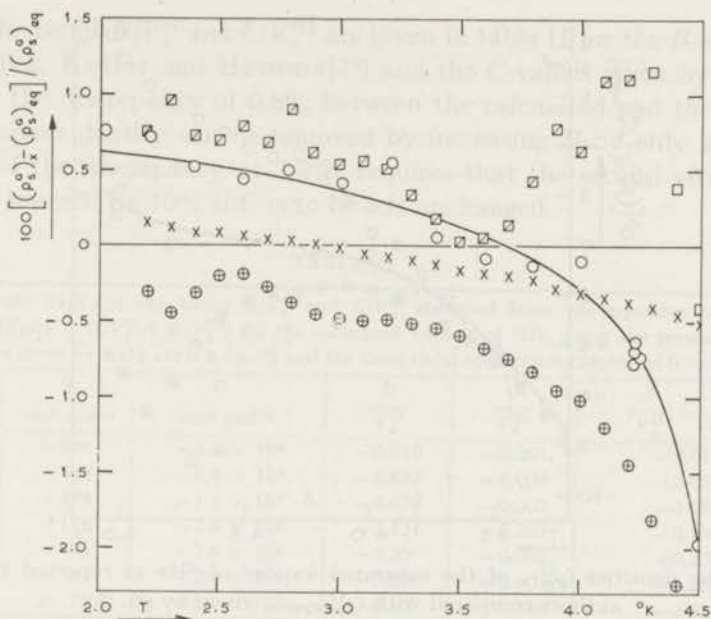


Fig. 2. The densities $(\rho_s^G)_x$ of the saturated vapour of ^4He obtained from this research as well as from data of other sources compared with $(\rho_s^G)_{\text{eq}}$ calculated from the equation of state using the virial coefficients given by eqs. (3) and (4).

- This research (direct method)
- Edwards⁶⁾ (refractive index, $N_A\alpha = 0.12427 \text{ cm}^3/\text{mol}$)
- ◻ Edwards and Woodbury⁷⁾ (refractive index, $N_A\alpha = 0.12427 \text{ cm}^3/\text{mol}$)
- ⊙ Ter Harmsel *e.a.*¹¹⁾ (calculated from eq. (2))
- × Calculated from the equation of state using the second virial coefficients reported by Kilpatrick *e.a.*¹⁶⁾ and the third virial coefficients given by eq. (5).

The smooth curve represents the average of the experimental points of the present research.

Above 3.5°K , however, ρ_s^G could be approximated by the equation

$$(\rho_s^G)_{\text{approx}} = F_1(T) - A_o(p_c - p_s)^\alpha - B_o(p_c - p_s)^\gamma \quad (6)$$

where

$$F_1(T) = (0.06969 - 0.001555(T - 5)) \text{ g cm}^{-3} \quad (T \text{ in } ^\circ\text{K})$$

$$A_o = 0.00420513 \text{ g cm}^{-3} \text{ mm Hg}^{-\alpha}$$

$$\alpha = 0.361$$

$$B_o = 3.47 \times 10^{-7} \text{ g cm}^{-3} \text{ mm Hg}^{-\gamma}$$

$$\gamma = 1.37.$$

The critical pressure, p_c , is taken to be 1705.0 mm Hg at 0°C and standard gravity⁹⁾. Eq. (6) is similar to eq. (7) in chapter I.

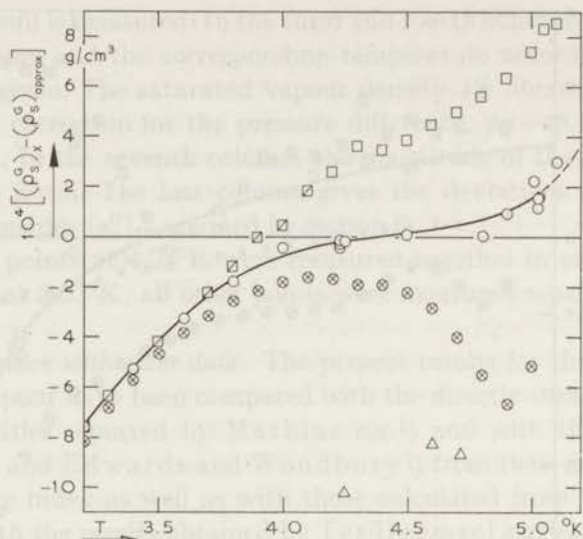


Fig. 3. The densities $(\rho_s^G)_x$ of the saturated vapour of ^4He as reported by various authors compared with $(\rho_s^G)_{\text{approx}}$ given by eq. (6).

- This research
- △ Mathias *e.a.*¹⁾
- Edwards and Woodbury⁷⁾
- ⊗ Ter Harmsel *e.a.*¹¹⁾

The smooth curve represents the average of the experimental points of the present research.

In fig. 3 the differences $\rho_s^G - (\rho_s^G)_{\text{approx}}$ are shown for data from various sources.

7. *Discussion.* At temperatures up to 3.8°K (see fig. 2) the results of the present research are in good agreement with the vapour densities derived from the refractive index measurements of Edwards⁶⁾ and Edwards and Woodbury⁷⁾ if the molar polarizability $N_A\alpha$ is taken equal to 0.12427 cm³/mol (see chapter I). Above 3.8°K differences up to 1% do occur (figs. 2 and 3), the densities derived from the refractive index measurements being higher than the present results. A possible explanation for these differences was given in chapter I.

The differences between the densities of the saturated vapour obtained from the present research and those reported by Mathias *e.a.*¹⁾ might be explained by the uncertainty of these authors about the temperature of the saturated vapour and the temperature of the vessel in which the gas was measured.

At temperatures below 4.2°K the present results agree to within 0.7% or better with the saturated vapour densities calculated from the equation of state. To show the influence of the virial coefficients on the calculated

density the terms B/V_s^G and $C/V_s^{G^2}$ are given in table II for the B -values of Kilpatrick, Keller and Hammel¹⁶⁾ and the C -values given by eq. (5). At 4.2°K the discrepancy of 0.6% between the calculated and the experimental vapour density can be removed by increasing B by only 2%. The removal of the discrepancy at 2.2°K requires that the second virial coefficient be lowered by 10% if C is to be left unchanged.

TABLE II

Approximate data for the terms B/V_s^G and $C/V_s^{G^2}$ deduced from the equation of state $p_s V_s^G = RT_{58}(1 + B/V_s^G + C/V_s^{G^2})$ for the saturated vapour of ^4He , using the second virial coefficients given by Kilpatrick <i>e.a.</i> ¹⁶⁾ and the third virial coefficients calculated from eq. (5).					
T_{58} °K	B $\text{cm}^3 \text{mol}^{-1}$	C $\text{cm}^6 \text{mol}^{-2}$	$\frac{B}{V_s^G}$	$\frac{C}{V_s^{G^2}}$	$\frac{B}{V_s^G} + \frac{C}{V_s^{G^2}}$
1.5	-264	-4.4×10^5	-0.010	-0.001	-0.011
2.0	-188	-5.8×10^4	-0.037	-0.002	-0.039
2.5	-144	-1.1×10^4	-0.078	-0.003	-0.081
3.0	-116	-2.6×10^3	-0.131	-0.003	-0.134
3.5	-96	-3.6×10^2	-0.20	-0.002	-0.20
4.0	-82	$+2.9 \times 10^2$	-0.28	+0.003	-0.28
4.5	-70	$+5.1 \times 10^2$	-0.40	+0.016	-0.38

Recently Grimsrud and Werntz¹⁸⁾ published new values for the second virial coefficient derived from measurements of the velocity of sound in ^4He gas between 2.0 and 3.8°K. No values of the third virial coefficient were reported. For the second virial coefficient the equation $B = ((22 \pm 4) - (433 \pm 22)/T) \text{cm}^3/\text{mol}$ was given. The B -value according to this equation is at 3.8°K 5% lower than that given by Kilpatrick *e.a.* and at 2.2°K the difference is 7% in the same direction. Obviously, the results of the present research can only be used to calculate the term $B + C/V_s^G + \dots$ and not B itself. However the B -values given by Grimsrud and Werntz are not confirmed by the present results, unless the C -values given by eq. (4) or eq. (5) are far too small.

It was mentioned that for the calculations of the saturated vapour density from the equation of state the T_{58} -scale was used for the relation between the vapour pressure and the temperature. Recently, suggestions¹⁹⁾²⁰⁾²¹⁾²²⁾ have been made that the thermodynamic temperature might be about 0.2% higher than T_{58} . This would decrease the calculated density by 0.2% and consequently lead to slightly larger differences between the calculated and the measured densities.

There is a systematic difference amounting, on the average, to about 1% between the present results and the saturated vapour densities calculated by Ter Harmsel *e.a.*¹¹⁾ from the apparent heat of vaporization of ^4He and the 1958- ^4He vapour pressure-temperature relation using eq. (2). At the present time no explanation can be given for this difference which is larger than the combined estimated error in ρ_s^G , L_a , T_{58} and $d\rho_s/dT_{58}$.

TABLE III

Smoothed densities $(\rho_s^G)_{sm}$ and molar volumes $(V_s^G)_{sm} = (4.0026 \text{ g/mol})/(\rho_s^G)_{sm}$ of the saturated vapour of ^4He derived from this research					
T_{58} °K	$10^3(\rho_s^G)_{sm}$ g cm ⁻³	$(V_s^G)_{sm}$ cm ³ mol ⁻¹	T_{58} °K	$10^3(\rho_s^G)_{sm}$ g cm ⁻³	$(V_s^G)_{sm}$ cm ³ mol ⁻¹
2.00	0.7978	5017.0	3.60	9.079	440.86
2.05	0.9017	4438.9	3.65	9.571	418.20
2.10	1.0128	3952.0	3.70	10.084	396.93
2.15	1.1310	3539.0	3.75	10.619	376.93
2.20	1.2553	3188.6	3.80	11.177	358.11
2.25	1.3870	2885.8	3.85	11.758	340.42
2.30	1.5270	2621.2	3.90	12.363	323.76
2.35	1.6756	2388.8	3.95	12.995	308.01
2.40	1.8330	2183.6	4.00	13.655	293.12
2.45	1.9996	2001.7	4.05	14.346	279.00
2.50	2.1755	1839.9	4.10	15.071	265.58
2.55	2.3612	1695.2	4.15	15.830	252.85
2.60	2.5568	1565.5	4.20	16.625	240.76
2.65	2.7627	1448.8	4.25	17.458	229.27
2.70	2.9792	1343.5	4.30	18.335	218.30
2.75	3.2064	1248.3	4.35	19.258	207.84
2.80	3.4446	1162.0	4.40	20.234	197.82
2.85	3.6942	1083.5	4.45	21.264	188.23
2.90	3.9554	1011.9	4.50	22.356	179.04
2.95	4.2287	946.5	4.55	23.517	170.20
3.00	4.5143	886.6	4.60	24.753	161.70
3.05	4.8127	831.7	4.65	26.075	153.50
3.10	5.1244	781.09	4.70	27.495	145.58
3.15	5.4498	734.45	4.75	29.029	137.88
3.20	5.7894	691.37	4.80	30.696	130.39
3.25	6.1436	651.51	4.85	32.525	123.06
3.30	6.5128	614.57	4.90	34.555	115.83
3.35	6.8975	580.30	4.95	36.842	108.64
3.40	7.2985	548.41	5.00	39.479	101.39
3.45	7.7165	518.71	5.05	42.629	93.89
3.50	8.152	491.00	5.10	46.642	85.82
3.55	8.606	465.09	5.15	52.581	76.12

8. *Smoothed results.* Smoothed densities $(\rho_s^G)_{sm}$ and molar volumes $(V_s^G)_{sm}$ of the saturated vapour of ^4He are given in table III. The smoothed densities between 2.0 and 4.0°K were obtained by applying the corrections given by the curve in fig. 2 to the vapour densities calculated from the equation of state using the virial coefficients given by eqs. (3) and (4) and the T_{58} -scale. Between 4.0 and 5.15°K the smoothed densities were calculated from eq. (6); the necessary corrections being taken from the curve in fig. 3.

9. *Conclusion.* The smoothed values of the density of the saturated vapour of ^4He given in table III are the first complete set of data determined by direct measurements. They are estimated to be accurate within 0.3%.

The densities of the liquid under saturation pressure reported in chapter I

and the saturated vapour densities obtained from the present research agree within 0.2%, at temperatures below 4.0°K, with densities calculated from the refractive index of the liquid and vapour, using the Lorenz-Lorentz law and 0.12427 cm³/mol for the molar polarizability. This is within the limits of accuracy of the measurements. Differences between the measured densities and those calculated from the refractive index occur above 4.0°K, for the liquid as well for the vapour, and may be attributed to experimental errors, although it cannot be excluded that these differences are caused by changes in the molar polarizability or deviations from the Lorenz-Lorentz law. No evidence is found, however, for a dependence of the molar polarizability on the density as reported by Kerr and Sherman²³⁾ for ³He.

The differences between the measured saturated vapour densities and those calculated from the equation of state are small near 4.0°K but they increase to 0.7% at the lower temperatures. In view of the uncertainties in the available data for the virial coefficients of the gas, these deviations are not surprising. At temperatures above about 4.2°K it cannot be expected that the equation of state gives reliable data for the saturated vapour density not only because of the uncertainty in the second and third virial coefficients but also because of the scarcity of information about higher virial coefficients.

10. *The rectilinear diameter, the critical density and the coexistence curve near the critical temperature.* The discussion given in this section on the rectilinear diameter, the critical density and the coexistence curve near the critical temperature lies somewhat outside the scope of the foregoing discussions. Nevertheless, the considerations outlined in this section have been used to draw the smooth curves through the experimental points in fig. 5, chapter I and in fig. 3, especially the curves above 5.0°K.

The rectilinear diameter. It is well-known that above the λ -point $(\rho_s^L + \rho_s^G)/2$ as a function of temperature can be approximated by a straight line, usually referred to as the rectilinear diameter. Several empirical equations were suggested^{1) 3) 7) 24)} for its representation.

An approximate rectilinear diameter was derived graphically from the experimental data for ρ_s^L (chapter I, table I) and ρ_s^G (table I) and was represented by the equation

$$F_1(T) = (0.06969 - 0.001555(T - 5)) \text{ g cm}^{-3}.$$

Furthermore, it was found that the densities ρ_s^L and ρ_s^G at temperatures between 4.0 and 5.1°K could be approximated by the equations

$$(\rho_s^L)_{\text{approx}} = F_1(T) + A_o(p_c - p_s)^\alpha + B_o(p_c - p_s)^\gamma \quad (7)$$

$$(\rho_s^G)_{\text{approx}} = F_1(T) - A_o(p_c - p_s)^\alpha - B_o(p_c - p_s)^\gamma \quad (6)$$

(see section 6, chapter I and section 7).

The experimental points and the smooth curves for the densities of the liquid and the saturated vapour (which were given in fig. 5 of chapter I and in fig. 3) are shown together in fig. 4. Curve *C*, lying half-way between *A* and *B*, represents $(\rho_s^L + \rho_s^G)/2 - F_1(T)$. It is evident from fig. 4 that the measured points for the densities of the liquid and the vapour determine the curves *A*, *B* and *C* and consequently $(\rho_s^L + \rho_s^G)/2$ only up to about 5.0°K.

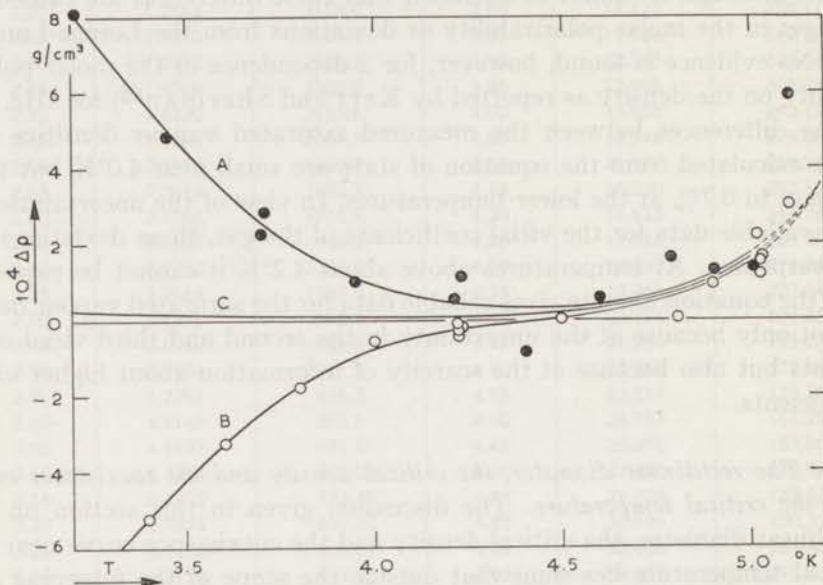


Fig. 4. Saturated liquid and vapour densities of ^4He and the "rectilinear diameter".

The following quantities are plotted along the ordinate:

- and curve *A*: $\rho_s^L - (\rho_s^L)_{\text{approx}}$ (see eq. (7))
- and curve *B*: $\rho_s^G - (\rho_s^G)_{\text{approx}}$ (see eq. (6))
- Curve *C*: $(\rho_s^L + \rho_s^G)/2 - (0.06969 - 0.001555(T - 5)) \text{ g cm}^{-3}$
(the slope of curve *C* at T_c is $0.001555 \text{ g cm}^{-3} \text{ }^\circ\text{K}^{-1}$)

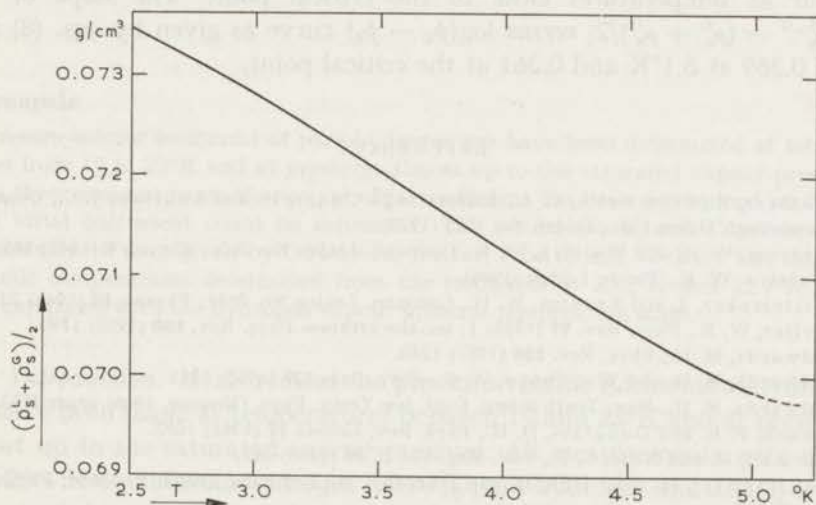
It may be mentioned here that the smooth curves for the liquid and vapour densities in fig. 5 of chapter I and in fig. 3 were not drawn independently but, in fact, were taken from fig. 4.

The critical density. An attempt has been made to extrapolate curve *C* to the critical temperature using the assumption, also made by other authors^{9) 25) 26)}, that $(\rho_s^L + \rho_s^G)/2$ is constant and equal to the critical density ρ_c at temperatures close to the critical point. The slope of curve *C* at the critical temperature is fixed by this assumption.

The extrapolation of curve *C* on this basis is shown in fig. 4. From curve *C* one obtains $\rho_c - F_1(T) = 0.00036 \text{ g cm}^{-3}$, which gives $\rho_c = 0.06976 \text{ g cm}^{-3}$ for $T_c = 5.189^\circ\text{K}$ ⁹⁾. The estimated accuracy of this value is 0.00020

TABLE IV

The critical density ρ_c of ^4He reported by various authors	
Source	ρ_c (g cm $^{-3}$)
Mathias <i>c.a.</i> ¹⁾	0.0693
Walstra ³⁾	0.06953
Kerr ²⁴⁾	0.0675 \pm 0.0005
Berman and Mate ¹⁰⁾	0.0680 \pm 0.0003
Edwards and Woodbury ⁷⁾ ($N_A\alpha = 0.12427$ cm 3 /mol)	0.06963 \pm 0.00030
Edwards ⁸⁾ (analyzed by Roach and Douglass ⁹⁾)	0.0697
Roach and Douglass ⁹⁾	0.0701 \pm 0.0006
Roach and Douglass ²⁶⁾	0.0690 \pm 0.0005
This research	0.06976 \pm 0.00020

Fig. 5. The rectilinear diameter of ^4He derived from the present results.

g cm $^{-3}$. Data for ρ_c reported by other authors are given in table IV. $(\rho_s^L + \rho_s^G)/2$ as a function of T between 2.5°K and the critical point is shown in fig. 5.

The coexistence curve above 4.4°K. At the critical point curves A and B should join curve C because the last two terms in eqs. (7) and (6) vanish at $p_s = p_c$. A possible extrapolation of curves A and B is shown in fig. 4. This extrapolation was used to obtain the smoothed values for ρ_s^L and ρ_s^G above 5.0°K (see table II, chapter I and table III).

Above 4.4°K ρ_s^L and ρ_s^G , as given by curves A and B respectively, can be described to a good approximation by the equations

$$\rho_s^L = (\rho_s^G + \rho_s^L)/2 + A_o(p_c - p_s)^\alpha + B_o(p_c - p_s)^\gamma \quad (8)$$

$$\rho_s^G = (\rho_s^L + \rho_s^G)/2 - A_o(p_c - p_s)^\alpha - B_o(p_c - p_s)^\gamma \quad (9)$$

where

$$(\rho_s^L + \rho_s^G)/2 = (0.06969 - 0.001555(T - 5) + \delta) \text{ g cm}^{-3}.$$

A_o , B_o , α and γ have the values given in section 6 and δ is a small correction term given by curve C in fig. 4.

It may be remarked that the extrapolations of curves A and B , and eqs. (8) and (9) are in accordance with the conclusion of Roach and Douglass⁹⁾ 26) that the exponent β_p , often used to characterize the coexistence curve near the critical temperature and defined by the relation

$$|\rho_s^{L,G} - (\rho_s^L + \rho_s^G)/2| = a(p_c - p_s)^{\beta_p},$$

does not change appreciably above 5.1°K and has a value between 0.382 and 0.355. This conclusion was deduced from measurements of the dielectric constant and the refractive index of the liquid and the saturated vapour at temperatures close to the critical point. The slope of the $\log |\rho_s^{L,G} - (\rho_s^L + \rho_s^G)/2|$ versus $\log(p_c - p_s)$ curve as given by eqs. (8) and (9) is 0.369 at 5.1°K and 0.361 at the critical point.

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CHAPTER III

PRESSURE-VOLUME ISOTHERMS OF HYDROGEN GAS BETWEEN 19 AND 23°K

Synopsis

Pressure-volume isotherms of para-hydrogen gas have been determined at temperatures from 19 to 23°K and at pressures almost up to the saturated vapour pressure. From these measurements the second virial coefficient has been determined while the third virial coefficient could be estimated. The results for B and C are in good agreement with data given by Goodwin, Diller, Roder and Weber. The thermodynamic temperatures determined from the isotherms at 23.3°K and 22.7°K have been compared with the hydrogen vapour pressure-temperature scale.

1. *Introduction.* Measurements on pressure-volume isotherms of hydrogen gas have been made at temperatures between 19 and 23°K and at pressures almost up to the saturated vapour pressure. All measurements were made with 20.4°K-equilibrium hydrogen (99.79% para-hydrogen and 0.21% ortho-hydrogen), hereafter referred to as equilibrium hydrogen or $e\text{-H}_2$.

In the temperature and pressure ranges employed the isotherms may be described by the equation of state

$$pV = RT(1 + B/V + C/V^2) \quad (1)$$

where p is the pressure, V the molar volume, R the molar gas constant, T the thermodynamic temperature, B the second virial coefficient and C the third virial coefficient.

Data for the virial coefficients of normal hydrogen (75% ortho- H_2 , 25% para- H_2), based on an analysis of data reported in the literature, were given in 1948 by Woolley, Scott and Brickwedde¹) in a review article on thermodynamic properties of hydrogen. Later, Beenakker, Varekamp and Van Itterbeek²) determined the second virial coefficient of normal hydrogen gas at 20.4°K and critically examined earlier measurements. Varekamp and Beenakker³) and Knaap, Knoester, Knobler and Beenakker⁴) made measurements on isotherms of normal hydrogen from 14 to 20°K and from 20 to 70°K, respectively, using a differential method.

Essentially, these authors determined $B(T) - B_{20.4^\circ\text{K}}$. Knaap *e.a.*⁴⁾ gave a table of B -values from 14 to 65°K based on the data for $B(T) - B_{20.4^\circ\text{K}}$ mentioned above and on the values for $B_{20.4^\circ\text{K}}$ given by Beenakker *e.a.*²⁾ and Van Agt and Kamerling Onnes (see refs. 4 and 5). Beenakker, Varekamp and Knaap⁶⁾ measured the difference between the second virial coefficients of normal hydrogen and equilibrium hydrogen. Recently Goodwin, Diller, Roder and Weber⁷⁾ published data for B and C of equilibrium hydrogen based, at temperatures above 24°K, on their own measurements and at temperatures below 23°K, on extrapolations and the B -values reported by Woolley *e.a.*¹⁾.

The present determinations of the isotherms of equilibrium hydrogen gas below 24°K were made to allow discrimination between the data for the virial coefficients given by different authors. The emphasis was laid on the range of relatively high pressures in order to obtain information about the third virial coefficient and because it was important to determine the density of the saturated vapour, which may be used for the calculation of the vapour pressure-temperature relation if the apparent heat of vaporization is known⁸⁾⁹⁾. This relation is of importance for temperature measurements and for the definition of an International Practical Scale of Temperature down to 13.8°K.

2. *Experimental equipment.* The apparatus consisted of a copper pycnometer of a nominal volume of 17 cm³, connected to a manometer system and to a gas-metering system. The gas-metering system consisted of four thermostated glass bulbs of nominal volumes of 5, 15, 50 and 300 cm³ and a constant volume manometer. The temperature of the pycnometer was measured with a germanium thermometer which was calibrated against the hydrogen vapour pressure scale (see section 4). The temperature of the gas in the capillary leading to the pycnometer was measured with gold-iron *versus* chromel thermocouples. The apparatus was previously used for measurements of the densities of liquid helium and helium vapour, and it was described in detail in chapters I and II.

3. *Experimental procedure.* Before starting a series of measurements, normal hydrogen was converted into equilibrium hydrogen in a separate vessel containing ferric oxide as a catalyst. The composition of the converted hydrogen was checked by comparing its vapour pressure with that of freshly liquefied normal hydrogen. The para-hydrogen concentration appeared always to be higher than 99%.

At the beginning of the determination of an isotherm a small amount of hydrogen exchange gas was admitted into the jacket of the capillary leading to the pycnometer (see fig. 1, chapter I). After cooling the apparatus to hydrogen temperatures, about 0.1 g of equilibrium hydrogen was condensed

in the pycnometer. The temperature of the hydrogen bath was adjusted to a desired value and maintained thereafter as nearly constant as possible. The resistance of the germanium thermometer and the vapour pressure of the condensed equilibrium hydrogen were measured. Following this, the liquid hydrogen in the pycnometer was pumped off and the pressure was adjusted to a value slightly less than the saturation pressure by using an oil differential manometer which indicated the difference between the pressure over the bath and the pressure in the pycnometer. Then, the pressure in the pycnometer and the resistance of the germanium thermometer were determined simultaneously under equilibrium conditions. After this, the gas-metering system described in chapter II (fig. 1) was evacuated. The gas in the pycnometer was successively expanded into the glass bulbs, the pressure in the system (pycnometer and glass bulbs) and the resistance of the germanium thermometer being measured after each expansion. When the measurement of the last point on the isotherm had been completed, the total amount of gas was determined at room temperature.

4. *Data reduction.* *a.* Reduction of measured pressures. The measured pressures were reduced to mm Hg at 0°C and standard gravity (1 mm Hg at 0°C and standard gravity = 133.322 N/m²). Corrections were applied for the thermomolecular pressure effect and the "aerostatic" pressure head of the gas in the capillary leading to the pycnometer.

b. Gas metering. The number of moles of gas at room temperature was calculated from the pressure, the temperature and the volume of the gas using the equation of state with data for the second virial coefficient given by Goodwin *et al.* (7). The molar gas constant was taken to be 8.3143 J/mol °K.

c. The temperature. Temperatures T_{L60} (T , Leiden, 1960)^{10) 11)} were obtained from the vapour pressure of equilibrium hydrogen using the relation

$$^{10}\log p = 4.635384 - 44.2674/T_{L60} + 0.021669 T_{L60} - 0.000021 T_{L60}^2 \quad (2)$$

where p is expressed in mm Hg at 0°C. As was mentioned before, the vapour pressure was measured at the beginning of the determination of each isotherm, using the pycnometer as a vapour pressure thermometer.

Due to a small drift of the temperature of the bath, the temperature of the pycnometer changed a few millidegrees during the measurements. Because the germanium thermometer was calibrated against the vapour pressure scale at the beginning of the determination of each isotherm, these small temperature changes could be calculated from the changes in the resistance R of the germanium thermometer and dR/dT obtained from previous calibrations of the thermometer between 14 and 24°K.

5. *Experimental results.* The measured molar volumes V_m at the pressures p_m , the saturated vapour pressures p_s and the corresponding temperatures T_{L60} are listed in table I.

TABLE I

Measured molar volumes, V_m , of equilibrium hydrogen gas at pressures p_m . The saturated vapour pressures, p_s , and the corresponding temperatures T_{L60} are also given.							
p_m mm Hg, 0°C	V_m cm ³ /mol	p_s mm Hg, 0°C	T_{L60} °K	p_m mm Hg, 0°C	V_m cm ³ /mol	p_s mm Hg, 0°C	T_{L60} °K
1681.6	724.7	1681.6	23.2681	1045.3	1121.3	1049.2	21.3995
1634.1	751.4	1677.4	23.2575	1015.6	1164.1	1048.3	21.3964
1610.6	764.8	1676.7	23.2558	821.75	1478.8	1047.6	21.3939
1532.0	812.4	1676.2	23.2545				
1326.1	962.8	1676.1	23.2543	781.44	1459.9	786.05	20.3743
710.07	1920.2	1676.6	23.2555	759.14	1513.8	785.70	20.3728
				747.96	1539.6	785.45	20.3717
1461.3	827.6	1464.6	22.6941	710.69	1629.9	784.92	20.3694
1419.0	858.2	1464.7	22.6944	614.62	1911.0	785.15	20.3704
1398.4	873.1	1462.4	22.6880	333.65	3647.5	783.61	20.3637
1328.9	927.6	1464.0	22.6924				
1148.1	1098.4	1463.4	22.6908	189.29	6566	785.82	20.3733
614.23	2178.1	1463.4	22.6908	75.99	16566	783.40	20.3628
1297.0	920.7	1300.1	22.2174	552.78	1992.4	557.65	19.2588
1258.7	957.1	1298.7	22.2131	537.54	2062.4	556.77	19.2539
1239.1	974.1	1292.9	22.1955	528.83	2095.1	550.43	19.2185
1177.7	1033.9	1292.3	22.1937	502.70	2213.1	547.94	19.2045
1017.5	1221.9	1292.2	22.1934	435.90	2579.4	546.34	19.1955
545.83	2403.5	1291.7	22.1919				
1135.9	1042.7	1144.7	21.7257				
1101.4	1082.8	1143.5	21.7218				
1085.1	1101.3	1142.4	21.7181				
1031.0	1168.0	1141.4	21.7148				
890.6	1377.6	1141.7	21.7158				
479.05	2687.7	1140.5	21.7118				

6. *Discussion.* In principle, the virial coefficients B and C and the thermodynamic temperature can be determined from the measured points along each isotherm, *e.g.*, by plotting $p_m V_m / R$ as a function of $1/V_m$. Instead of analyzing the results in this way, they have been compared with results calculated from the equation of state using the temperature T_{L60} as a provisional approximation of the thermodynamic temperature and values for the virial coefficients from different authors.

The calculations were performed firstly with values for B and C given by Goodwin *e.a.*⁷⁾ For each measured value of the molar volume V_m a pressure $p_{c,G}$ (p , calculated, Goodwin *e.a.*) was calculated using the equation

$$p_{c,G} V_m = RT_{L60} (1 + B_G / V_m + C_G / V_m^2) \quad (3)$$

where B_G and C_G are the virial coefficients as given by Goodwin *e.a.* Further, it was assumed that the experimental results could be described by

an equation of state

$$p_m V_m = RT_m (1 + B_m/V_m + C_m/V_m^2) \quad (4)$$

where T_m , B_m and C_m are the values for the thermodynamic temperature and the second and third virial coefficients which follow from the measurements. From eqs. (3) and (4) one obtains to a good approximation

$$\begin{aligned}
 (p_m - p_{c,G}) V_m / RT_{L60} = \\
 = (T_m - T_{L60}) / T_{L60} + (B_m - B_G) / V_m + (C_m - C_G) / V_m^2. \quad (5)
 \end{aligned}$$

In fig. 1 $(p_m - p_{c,G}) V_m / RT_{L60}$ is plotted as a function of $1/V_m$.

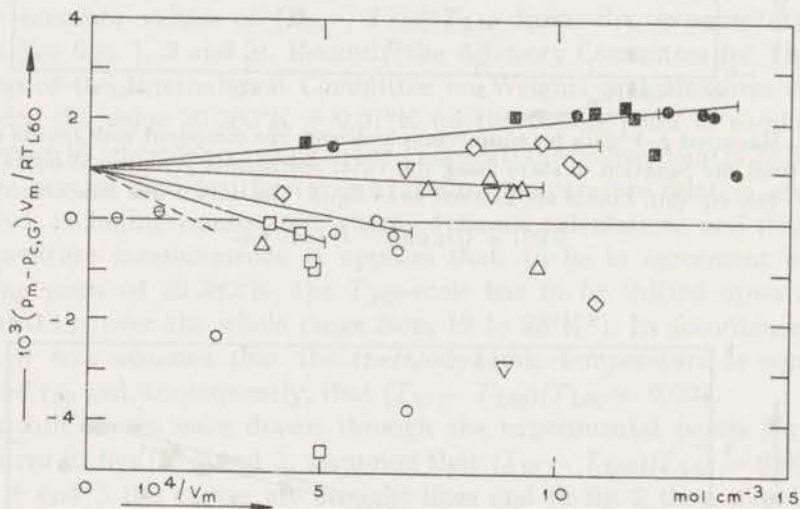


Fig. 1. Measured p - V data for equilibrium hydrogen gas compared with results calculated from the equation of state using the virial coefficients given by Goodwin *et al.* (see eq. (5)).

- | | |
|----------------------|----------------------|
| ● isotherm at 23.3°K | △ isotherm at 21.7°K |
| ■ " " 22.7°K | ▽ " " 21.4°K |
| ◇ " " 22.2°K | ○, ⊙ " " 20.4°K |
| | □ " " 19.2°K |

The curves are drawn through the experimental points for each isotherm and through the point $1/V_m = 0$, $(p_m - p_{c,G}) V_m / RT_{L60} = 0.001$. In some cases the points at two temperatures are represented by a single curve (23.3°K and 22.7°K; 21.7°K and 21.4°K).

The dotted line indicates $0.001 + (B_{KKKB} - B_G) / V_m$ where B_{KKKB} are the values of the second virial coefficient given by Knaap *et al.*⁴, recalculated to e -H₂. The vertical lines indicate the values of $1/V_{saturated}$ for each isotherm.

Similar calculations were made using the data for B and C given by Woolley, *et al.*¹). In this case

$$\begin{aligned}
 (p_m - p_{c,WSB}) V_m / RT_{L60} = \\
 = (T_m - T_{L60}) / T_{L60} + (B_m - B_{WSB}) / V_m + (C_m - C_{WSB}) / V_m^2. \quad (6)
 \end{aligned}$$

In fig. 2 $(p_m - p_{c,WSB}) V_m / RT_{L60}$ is plotted as a function of $1/V_m$.

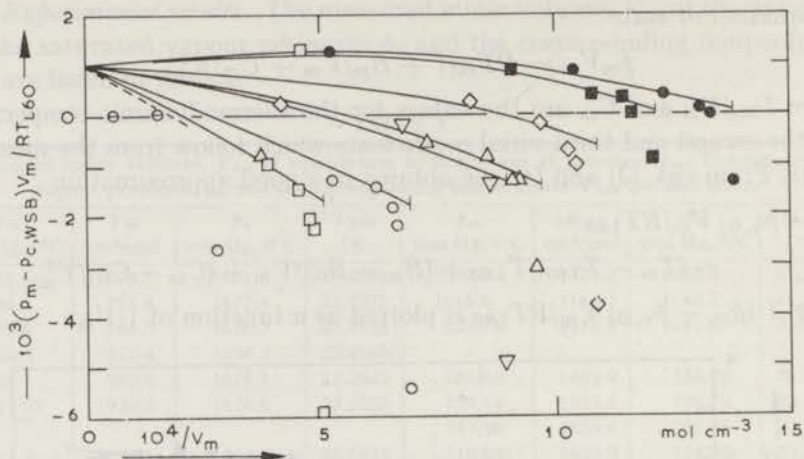


Fig. 2. Measured p - V data for equilibrium hydrogen gas compared with results calculated from the equation of state using the virial coefficients given by Woolley *et al.* (see eq. (6)). Points are marked as in fig. 1. The dotted line indicates

$$0.001 + (B_{KKKB} - B_{WSB})/V_m.$$

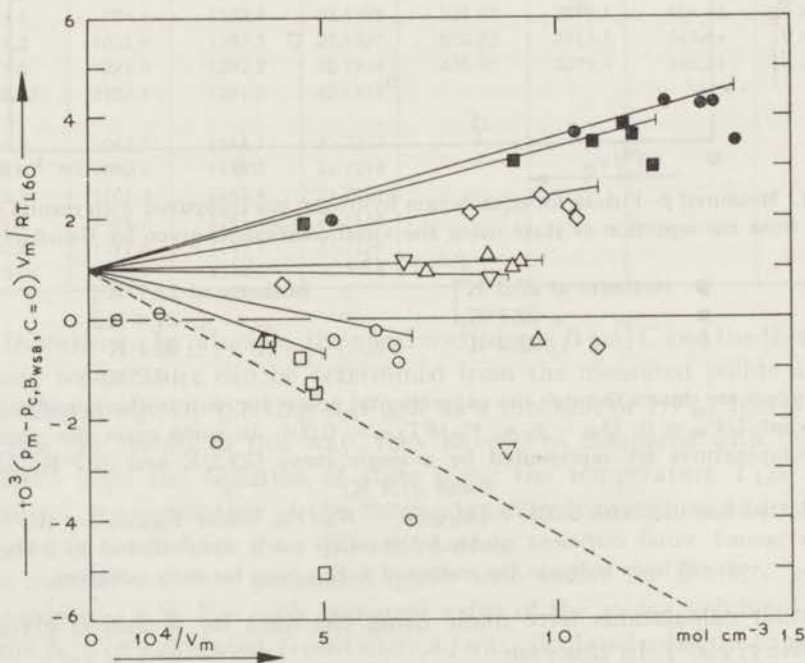


Fig. 3. Measured p - V data for equilibrium hydrogen gas compared with results calculated from the equation of state using B according to Woolley *et al.* and $C = 0$ (see eq. (7)). Points are marked as in fig. 1. The dotted line indicates

$$0.001 + (B_{KKKB} - B_{WSB})/V_m.$$

Finally, the calculations were made using the B -values according to Woolley *e.a.* and $C = 0$. In this case

$$(\hat{p}_m - \hat{p}_{c, B_{\text{WSB}}, C=0}) V_m / RT_{L60} = (T_m - T_{L60}) / T_{L60} + (B_m - B_{\text{WSB}}) / V_m + C_m / V_m^2 \quad (7)$$

The results for $(\hat{p}_m - \hat{p}_{c, B_{\text{WSB}}, C=0}) V_m / RT_{L60}$ are shown in fig. 3.

The B -values given by Woolley *e.a.* for normal hydrogen were recalculated to equilibrium hydrogen using $B_{n-H_2} - B_{e-H_2} = (6.22 - 0.23 T) \text{ cm}^3/\text{mol}$ (6) 8) 9).

The scarcity of points at low pressures makes it difficult to obtain very accurate values of $(T_m - T_{L60}) / T_{L60}$ from the experimental results (see figs. 1, 2 and 3). Recently the Advisory Committee for Thermometry of the International Committee on Weights and Measures recommended the value $20.280^\circ\text{K} \pm 0.01^\circ\text{K}$ for the boiling point of equilibrium hydrogen¹²⁾ whereas according to the T_{L60} -scale the boiling point is 20.260°K . When several data for the vapour pressure temperature relation are considered, including results from thermodynamic calculations and magnetic temperature measurements, it appears that, to be in agreement with a boiling point of 20.280°K , the T_{L60} -scale has to be shifted upwards by about 0.1% over the whole range from 19 to 23°K *). In accordance with this, it was assumed that the thermodynamic temperature is equal to $1.001 T_{L60}$ and, consequently, that $(T_m - T_{L60}) / T_{L60} = 0.001$.

Smooth curves were drawn through the experimental points for each isotherm in figs. 1, 2 and 3, assuming that $(T_m - T_{L60}) / T_{L60} = 0.001$. In figs. 1 and 3 the curves are straight lines and in fig. 2 they show slight curvature.

It can be seen that in the region of the saturation pressure the points deviate considerably from the smooth curves. These deviations have been attributed to adsorption of hydrogen at the wall of the pycnometer (see section 8).

The differences between the measured virial coefficients (B_m and C_m) and the values of the virial coefficients used in the calculations can be obtained from the slopes of the curves at $1/V_m = 0$ and from their deviations from linearity. In the figures are indicated also the slopes which the curves would have at $1/V_m = 0$ if the present results were in agreement with the B -values given by Knaap *e.a.* 4) (B_{KKKB}) recalculated to equilibrium hydrogen using $B_{n-H_2} - B_{e-H_2} = (6.22 - 0.23 T) \text{ cm}^3/\text{mol}$. These B -values are about $5.3 \text{ cm}^3/\text{mol}$ lower than those given by Goodwin *e.a.* For comparison, different values for B and C are given in table II and shown in figs. 4 and 5.

) In the temperature range under consideration a temperature T^ defined by the relation $T^* = T_{L60} + 0.001 T_{L60}$ is, within a few millidegrees, in agreement with the recently proposed International Practical Scale of Temperature (Travaux du Comité Consultatif de Thermométrie, Session 1967, to be published by the International Bureau of Weights and Measures, Sèvres, France).

TABLE II

The virial coefficients of equilibrium hydrogen						
T_{L60} °K	B cm ³ /mol				C cm ⁶ /mol ²	
	Woolley <i>e.a.</i>	Knaap <i>e.a.</i>	Goodwin <i>e.a.</i>	present research	Woolley <i>e.a.</i>	Goodwin <i>e.a.</i>
23.26	-118.7	-124.0	-118.3	-117.3	2559	1088
22.69	-123.0	-128.3	-122.7	-121.7	2651	925
22.19	-126.9	-132.2	-126.8	-126.3	2739	754
21.71	-130.8	-136.2	-130.9	-131.2	2828	561
21.40	-133.6	-138.9	-133.7	-134.0	2888	420
20.37	-143.3	-148.8	-143.6	(-145.3)	3106	-153
19.26	-155.3	-160.5	-155.7	(-158.5)	3372	-1000

Woolley *e.a.* and Knaap *e.a.* gave data for normal hydrogen; the values for B given here have been recalculated to *e*-H₂.
 The data from Knaap *e.a.* depend on their adopted value for B at 20.4°K, and therefore they may be shifted by a constant amount.
 Values between brackets are probably less accurate.

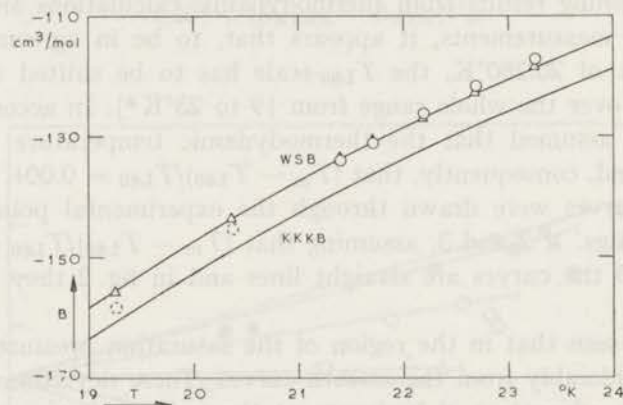


Fig. 4. The second virial coefficient of equilibrium hydrogen gas.

WSB: Woolley, Scott and Brickwedde.

KKKB: Knaap, Knoester, Knobler and Beenakker.

△ Goodwin, Diller, Roder and Weber.

○ present results obtained from the slopes of the curves in fig. 1.

7. *Conclusion.* The following conclusions may be drawn from the figures.

1. The third virial coefficient. The fact that the experimental points in fig. 1 can be represented by straight lines shows that the measured isotherms are in agreement, within the accuracy of the measurements, with the third virial coefficients given by Goodwin *e.a.*⁷⁾ It can be seen from fig. 3, however, that the present results show no evidence that a third virial coefficient is necessary to describe the isotherms. In fact, the term C/V^2 , where C is taken from Goodwin *e.a.*, is very small; even at saturation

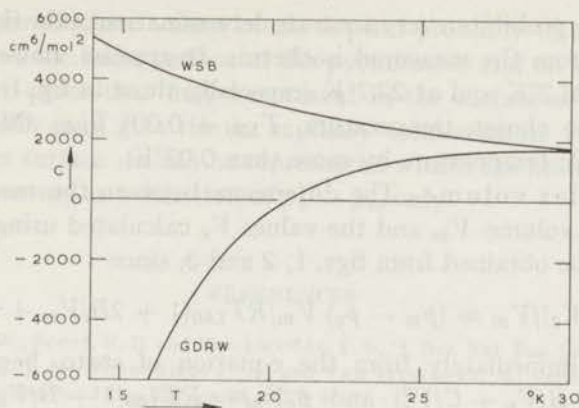


Fig. 5. The third virial coefficient of hydrogen gas.
 WSB: Woolley, Scott and Brickwedde.
 GDRW: Goodwin, Diller, Roder and Weber.

pressure at 23.2°K it does not exceed 0.002. Mainly because the values for C given by Goodwin *e.a.* are a smooth extrapolation of results for C obtained above 24°K, they may be preferred to $C = 0$.

The lines in fig. 2 are not straight and this indicates that the present results do not confirm the data for the third virial coefficient given by Woolley *e.a.* It may be mentioned that the latter results were obtained from data above 30°K by extrapolation, assuming that $CT^{\frac{1}{2}}$ is approximately constant.

2. The second virial coefficient. Values for the second virial coefficient were deduced from the slopes of the curves in fig. 1. They are given in table II and in fig. 4. The accuracy of the results may be judged from fig. 1. For the temperatures from 23.2°K to 21.4°K the accuracy in B is estimated to be 1%. For the 20.4°K and 19.2°K isotherms the choice of the points at $1/V_m = 0$ (this means the choice of the thermodynamic temperature of the isotherm) influences the results for B significantly. Therefore, the accuracy of the B -values obtained from these two isotherms is estimated to be 2%.

It can be seen from table II (and, in fact, also from fig. 1) that the present results for B agree closely with the data given by Goodwin *e.a.*⁷⁾ (or with those given by Woolley *e.a.*¹⁾, especially at temperatures from 23.2°K to 21.4°K, where the determination of B was more accurate than at the two lower temperatures.

The data for B from Knaap *e.a.*⁴⁾ (recalculated to $e-H_2$) depend on their adopted value for B at 20.4°K (see section 1) and can be brought into agreement with the present results and with the data of Goodwin *e.a.*⁷⁾ by shifting them systematically upwards by 5 cm^3/mol (see table II).

3. The temperature. It has been mentioned that the scarcity of low

pressure points prohibits a very accurate determination of the thermodynamic temperature from the measured isotherms. It appears, however, from the isotherms at 23.2°K and at 22.7°K (especially those in fig. 1) that it is unlikely that the chosen temperature, $T_{L60} + 0.001 T_{L60}$, differs from the thermodynamic temperature by more than 0.02°K.

4. The molar volume. The differences between the measured values of the molar volume V_m and the values V_c calculated using the equation of state may be obtained from figs. 1, 2 and 3, since

$$(V_m - V_c)/V_m \approx (p_m - p_c) V_m / RT_{L60}(1 + 2B/V_m + 3C/V_m^2). \quad (8)$$

This follows immediately from the equation of state, because $p_m V_c = RT_{L60}(1 + B/V_c + C/V_c^2)$ and $p_c V_m = RT_{L60}(1 + B/V_m + C/V_m^2)$ so that $(p_m - p_c)/(V_c - V_m) \approx (\partial p/\partial V)_T$.

The value of the factor $1 + 2B/V_m + 3C/V_m^2$ in eq. (8) is always between 1 and 0.6 in the pressure and temperature ranges employed. It follows from fig. 1 and eq. (8) that the differences between the measured molar volumes and those calculated using for B and C the data given by Goodwin *et al.*⁷⁾ and using T^* for the temperature ($T^* = T_{L60} + 0.001 T_{L60}$) are less than 0.2% for all isotherms.

8. Adsorption at pressures close to saturation. Assuming that at pressures close to saturation the deviations of the experimental points from the smooth curves (see figs. 1, 2 and 3) are due to adsorption, the number of moles of adsorbed hydrogen Δn can be calculated from the relation

$$\Delta n \approx (v_{\text{vessel}}/V_m) \delta / (1 + 2B/V_m + 3C/V_m^2)$$

where v_{vessel} is the volume of the pycnometer and δ is the deviation of the points (in fig. 1) from the smooth curves. In fig. 6 Δn is given as a function

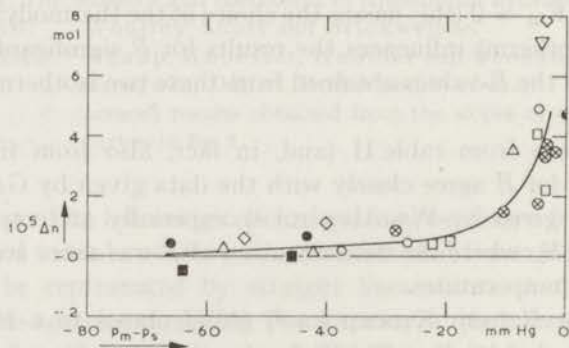


Fig. 6. The number of moles Δn of hydrogen adsorbed in the copper pycnometers (volume 17 cm³) at pressures p_m close to the saturated vapour pressure p_s , as a function of $p_m - p_s$. The points are marked as in fig. 1 (\oplus points calculated from an isotherm at 17.8°K).

of $p_s - p_m$. The absolute values of Δn depend probably to a large extent on the nature of the inner surface of the pycnometer and on the size distribution of micro-pores that may be present in the surface or in the solder joints, and which may give rise to capillary condensation. It can be seen that for a given surface Δn can be represented within the limits of accuracy of the measurements as a function of $p_s - p_m$ only.

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SAMENVATTING

In dit proefschrift worden metingen beschreven van de dichtheid van vloeibaar en gasvormig ^4He en van waterstofgas bij lage temperaturen. De metingen zijn uitgevoerd door een gecalibreerde pycnometer met vloeistof of gas tot de gewenste druk te vullen en door daarna de hoeveelheid gas te meten die vrijkomt als de pycnometer tot kamertemperatuur wordt opgewarmd.

In het eerste hoofdstuk worden metingen vermeld van de dichtheid van vloeibaar ^4He onder een druk die iets hoger is dan de druk van de verzadigde damp en bij temperaturen tussen 1,2 en 5,1°K. Met behulp van gegevens over de isotherme compressibiliteit is de dichtheid van vloeibaar ^4He onder de druk van de verzadigde damp uit de gemeten dichtheid berekend. De resultaten zijn vermeld in tabel II, hoofdstuk I, en zijn vergeleken met die van andere onderzoekers (zie fig. 4 en 5, hoofdstuk I).

In het tweede hoofdstuk worden metingen besproken van de dichtheid van ^4He -gas bij drukken die iets lager zijn dan de verzadigingsdruk en bij temperaturen tussen 2,0 en 5,1°K. De dichtheid van de verzadigde damp is uit de gemeten dichtheid berekend met behulp van gegevens over de isotherme compressibiliteit van ^4He -gas. De resultaten zijn vermeld in tabel III, hoofdstuk II, en zijn vergeleken met oudere metingen en met dichtheden die berekend zijn met behulp van de toestandsvergelijking van heliumgas of de vergelijking van Clapeyron (zie fig. 2 en 3, hoofdstuk II).

Uitgaande van de in hoofdstuk I vermelde gegevens over de dichtheid van de vloeistof onder de verzadigingsdruk en van de in dit hoofdstuk verkregen resultaten betreffende de dichtheid van de verzadigde damp, is een beschouwing gegeven over de „rechtlijnige diameter” voor ^4He , (fig. 4 en 5, hoofdstuk II) waarna door extrapolatie naar het kritische punt voor de kritische dichtheid de waarde 0,06976 g/cm³ is gevonden.

Het derde hoofdstuk is gewijd aan bepalingen van isothermen van waterstofgas bij temperaturen tussen 19 en 23°K. De nadruk is gelegd op metingen

bij relatief hoge drukken, om de invloed van de derde viriaalcoëfficiënt te bestuderen en om in staat te zijn door extrapolatie de dichtheid van de verzadigde damp te bepalen. De verkregen resultaten zijn vergeleken met isothermen die berekend zijn met behulp van de toestandsvergelijking, waarbij verschillende in de literatuur opgegeven waarden voor de viriaalcoëfficiënten zijn gebruikt (zie fig. 1, 2, 3, 4 en 5, hoofdstuk III). Wanneer de door Goodwin, Diller, Roder en Weber opgegeven waarden voor de tweede en derde viriaalcoëfficiënt worden gebruikt, wordt een goede overeenstemming gevonden tussen de berekende isothermen en de gemeten isothermen.

CURRICULUM VITAE

At the request of the Faculty of Science of the State University of Leiden, a short account of my studies is given.

After receiving secondary education at Hantoub (Sudan) and obtaining a Sudan School Certificate of General Education in 1955, I was admitted to the Faculty of Science of the University of Khartoum where I studied mathematics, physics and chemistry. I was awarded a degree of Bachelor of Science in 1959 and proceeded to an advanced course in physics. Having passed the B.Sc. (Honours) Examination in physics in March, 1961, I was selected for a study term of one year in Eindhoven (The Netherlands), sponsored by N.V. Philips' Gloeilampenfabrieken. There I had the opportunity to follow lecture courses on general and industrial electronics and to carry out some experimental studies on various applications of Geiger-Müller and scintillation counters. My studies were rewarded with a Diploma of the Philips International Institute of Technological Studies (Eindhoven) in September, 1962.

I joined the Kamerlingh Onnes Laboratory of the State University of Leiden at the beginning of November, 1962, where the research work described in this thesis was performed at the thermometry section headed at first by Dr. H. van Dijk and afterwards by Dr. M. Durieux. On the 7th July, 1964, I obtained the degree of Doctorandus in physics at the State University of Leiden.

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