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THE HEAT OF VAPORIZATION OF
HYDROGEN AND OF HELIUM



H. TER HARMSEL

8 DEC 1964

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFIC. DR. J.A.M. HEDING,
HOOGLERAAR IN DE FACULTEIT DER GODGE-
LEERDHEID, TEN OVERGAVEN CONMISSIE
UIT DESENAAR

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LEERDHEID, TEN OVERSTAAN VAN EEN COMMISSIE
UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG
21 DECEMBER 1966 TE 15 UUR

DOOR
HEIN TER HARMSEL
GEBOREN TE RIJSSEN IN 1921

THE HEAT OF VAPORIZATION OF
HYDROGEN AND OF HELIUM

Promotor: Prof. Dr. C. J. Gorter.

Dit proefschrift is bewerkt onder toezicht van

Dr. H. van Dijk en Dr. M. Durieux.

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJSHOOGESCHOOL TE LEIDEN, OP DRAG VAN
DE RECTOR MAGISTRUS DR. K. A. H. BONGE,
HOOGLEERAR IN DE FACULTEIT DER GODGE-
LEERDHEID, TEN OVERSTAAN VAN EEN COMMISSIE
VUT DE ZAKAAT TE VERKRIJGEN OP WOENSDAG
21 OKTOBER 1926, TE 12 UUR

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Uitgegeven door de uitgeverij
van de Universiteit van Leiden

Tegelijk te voldoen aan het verzoek van de Faculteit der Wetenschappen en Natuurwetenschappen te Leiden om overzicht van mijn studie.

Na het afleggen van het eindexamen 1935-36 aan het Chr. Lyceum te Almelo in 1931 volgde ik de opleiding voor de afdeling Weg- en Waterbouwkunde van de P.T.S. aan de Universiteit te Amsterdam, welke opleiding in 1940 eigenliefde werd met het afleggen van het eindexamen. Vervolgens was ik tot eind 1940 werkzaam in het bedrijfsleven, waarna ik mijn studie van de High School te Leiden begon. In juli 1953 legde ik het eindexamen af en in juli 1953 het doctoraal examen experimentele natuurkunde af. Ter voorbereiding van het doctoraal examen volgde ik de colleges van Prof. Dr. S. B. de Groot, Prof. Dr. F. Masur, Dr. J. van Kranendonk en Ir. J. Roffers.

Hierna was ik sedert september 1953 werkzaam op de afdeling Thermometrie van het Kamerlingh Onnes Laboratorium. Onder leiding van Dr. H. van Dijk werkte ik hier aan verschillende onderzoeken op het gebied van de thermometrie. Daarnaast assisteerde ik Dr. M. Barthelemy bij deze magnetische temperatuurmetingen in het vloeistof helium gebied. Voorts heb ik bij de berekeningen voor de 1954-55 "De temperatuurschaal".

Hiel 1955 werd een begin gemaakt met de opbouw van de apparatuur voor de metingen van de verloopingscoëfficiënten van waterstof en helium. De in dit procesdrift verrichte onderzoeken werden voortzet onder leiding van Dr. H. van Dijk. Bij de afsluiting der metingen werd Dr. M. Barthelemy mij bevonden met raad en daad ter zijde, hetwelk veel heeft bijgedragen tot het volbrengen van deze onderzoeken. Bij de afsluiting der werkzaamheden werd ik bijgestaan door de heer J. Durrouzal, die de berekening van de $p-T$ relaties verrichtte op het Kamerlingh Onnes Instituut der High School te Leiden.

Bij de opbouw van de apparatuur en bij technische verzorging van de colleges ontving ik veel steun van de technische staf van het Kamerlingh Onnes Laboratorium. In het bijzonder naam ik de heren L. Kasebeem en J. J. van der Vliet, die de onderzoekingen cryogonisch verzorgden en de calibratiematen construeerden, en voorts de heren H. Kaspers, C. J. van Klink en H. Krol, die de glasapparatuur vervaardigden.

Van 1956 af tot 1958 was ik als assistent verbonden aan het natuurkundig practicum voor proefscholers. Deze taak werd gekornde 1959 en 1961 onderbroken om de verzorging van de "Communitatis officio" from the Kamerlingh Onnes Laboratory of the "Leiden" naar te nemen voor Dr. M. Barthelemy. Sedert heb ik deze werkzaamheden voortzet van twee zijden. De verzorging van de "Communitatis officio" geschiedt in samenwerking met M.J. C. Kasebeem.

Aan mijn moeder

Aan mijn vrouw

Teneinde te voldoen aan het verzoek van de Faculteit der Wetenschappen en Natuurwetenschappen volgt hier een overzicht van mijn studie.

Na het afleggen van het eindexamen HBS-B aan het Chr. Lyceum te Almelo in 1941 volgde ik de opleiding in de afdeling Weg- en Waterbouwkunde van de MTS (thans HTS) te Rotterdam, welke opleiding in 1945 afgesloten werd met het afleggen van het eindexamen. Vervolgens was ik tot eind 1950 werkzaam in het bedrijfsleven, waarna ik mijn studie aan de Rijksuniversiteit te Leiden begon. In juli 1955 legde ik het candidaatsexamen a en in juli 1959 het doctoraalexamen experimentele natuurkunde af. Ter voorbereiding van het doctoraalexamen volgde ik de colleges van Prof. Dr. S.R. de Groot, Prof. Dr. P. Mazur, Dr. J. van Kranendonk en Ir. J. Snijder.

Inmiddels was ik sedert september 1955 werkzaam op de afdeling Thermometrie van het Kamerlingh Onnes Laboratorium. Onder leiding van Dr. H. van Dijk werkte ik hier aan verschillende onderzoeken op het gebied van de thermometrie. Daarnaast assisteerde ik Dr. M. Durieux bij diens magnetische temperatuurmetingen in het vloeibaar helium gebied. Voorts hielp ik bij de berekeningen voor de 1958 - ^4He temperatuurschaal.

Eind 1960 werd een begin gemaakt met de opbouw van de apparatuur voor de metingen van de verdampingswarmten van waterstof en helium. De in dit proefschrift vermelde onderzoeken werden verricht onder leiding van Dr. H. van Dijk. Bij de uitvoering der metingen stond Dr. M. Durieux mij bovendien met raad en daad ter zijde, hetgeen veel heeft bijgedragen tot het welslagen van deze onderzoeken. Bij de uitwerking der meetresultaten werd ik bijgestaan door de heer J. Dorrepaal, die de berekening van de L_a -functies en de p-T relaties verrichtte op het Mathematisch Instituut der Rijksuniversiteit te Leiden.

Bij de opbouw van de apparatuur en bij de technische verzorging van de metingen ontving ik veel steun van de technische staf van het Kamerlingh Onnes Laboratorium. In het bijzonder noem ik de heren L. Neuteboom en J. Turenhoût, die de onderzoeken cryogeentechnisch verzorgden en de calorimeter construeerden, en voorts de heren H. Kuipers, C.J. van Klink en B. Kret, die de glasapparatuur vervaardigden.

Van 1956 af tot 1965 was ik als assistent verbonden aan het natuurkundig practicum voor praecandidaten. Deze taak werd gedurende 1960 en 1961 onderbroken om de verzorging van de "Communications from the Kamerlingh Onnes Laboratory of the University of Leiden" waar te nemen voor Dr. M. Durieux. Sedert februari 1965 heb ik deze werkzaamheden geheel van hem overgenomen. De verzorging van de "Communications" geschiedt in samenwerking met Mej. C. Kesseboom.

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CHAPTER I

INTRODUCTION AND SUMMARY

1. Introduction

The heat of vaporization of hydrogen and helium is not only important because it is one of the thermodynamic properties of the in low temperature physics most used liquified gases, but also for the derivation of vapour pressure-temperature relations (p - T relations) or for checking the consistency of the data for the virial coefficients of these gases with data obtained for the heat of vaporization, if the p - T relation is already known.

The heat of vaporization is related in a simple way to the derivative of the pressure of the saturated vapour of a liquid with respect to the thermodynamic temperature by means of Clapeyron's equation:

$$\frac{dp}{dT} = \frac{L}{T (V_G - V_L)} \quad (1)$$

In this equation L is the molar heat of vaporization, V_G is the molar volume of the saturated vapour and V_L is the molar volume of the liquid under its saturation pressure. L is the amount of heat required for the evaporation at constant temperature of one mole of liquid. Usually the heat is supplied by means of an electric heater, so that the resistance of this heater, the current and the time during which the heat is supplied, have to be measured. The resistance and the current can be measured with an accuracy of 0.005% or better. The time can be measured with a conventional stopwatch with an accuracy of 0.01%.

In some older investigations the amount of evaporated liquid was measured from the difference between the initial and the final height of the liquid level in a calibrated calorimeter, but as it is difficult to measure the height of the liquid level within 0.1 mm, while usually the difference between the initial and the final level is only a few cm, the accuracy of those measurements will not be better than 0.5 to 1%. Therefore, in later experiments, the apparent heat of vaporization L_a has been measured. L_a is the amount of heat required to liberate at constant temperature a mole of vapour from a calorimeter. There is a difference between L and L_a since in the definition of L_a the saturated vapour that occupies the space vacated by the liquid, is not included in the mole of vapour.

If the amount of evaporated liquid is n moles, then the volume of this space is nV_L . The amount of saturated vapour in this space is nV_L/V_G moles. When n_a is the amount of vapour liberated from the calorimeter, then $n_a = n - nV_L/V_G$, and therefore $L = L_a (1 - V_L/V_G)$.

If the pressure of the saturated vapour is high enough, the evaporated gas can be gathered easily in calibrated vessels at room temperature. The amount of vapour liberated from the calorimeter can be derived from the pressure, volume and temperature of the gas in the calibrated vessels, measured at room temperature. The accuracy for each of these quantities can be about 0.01%, so that, together with the error in the heat supply, the errors in the results of the L_a -measurements need not to exceed 0.05%. The experimental L_a -values can directly be used for the derivation of a p-T relation, as Clapeyron's equation can be written as:

$$\frac{d \ln p}{d T} = \frac{L_a}{RT^2 (1 + B/V_G + C/V_G^2)} \quad (2)$$

Equation (2) can be derived from equation (1) by substituting

$L = L_a (1 - V_L/V_G)$ and $V_G = RT (1 + B/V_G + C/V_G^2)/p$ in equation (1).

As V_G depends on p, $(d \ln p)/dT$ and $\ln p$ have been evaluated by iterative solution, starting with a provisional p-T relation for the evaluation of V_G . To calculate $\ln p$ a value for the temperature of the boiling point has to be adopted.

In equation (2) V_G enters only in the correction terms, therefore the calculations with equation (2) will require a smaller number of approximations than those with equation (1) to obtain a same accuracy in dp/dT and $\ln p$.

In addition to the possibility, given by equation (2) to use directly the experimental L_a -values, without calculating L from these values, another advantage of the use of L_a is the elimination of V_L from equation (1).

It is clear that by using different values for the temperature of the boiling point and different values for the virial coefficients, different p-T relations will result from the evaluation of equation (2).

In this thesis the results of accurate measurements of the apparent heat of vaporization of 20.4 °K-equilibrium hydrogen (0.21% ortho and 99.79% para hydrogen), here after called equilibrium hydrogen, between its triple point, 13.8 °K, and 24 °K, and of helium between 2.2 °K and 5 °K are given. Moreover, an accurate determination of the vapour pressure of equilibrium hydrogen at its triple point is reported.

2. Summary of the contents

The experimental equipment, consisting of the calorimeter assembly, the manometer system for measuring and regulating the pressure in the calorimeter during the evaporation, the system for measuring the amount of gas liberated from the calorimeter and the equipment for measuring the heat supply is described in chapter II.

In chapter II also the calibrations of the vessels in which the

gas was gathered, the calibration of the stopwatches, the accuracy of the pressure measurements and the procedure of an experiment are discussed.

In chapter III the results of the measurements of the apparent heat of vaporization and of the triple point pressure of equilibrium hydrogen are given. The derivation of several p-T relations for equilibrium hydrogen from the experimental L_a -values using eq. (2) with different values for the temperature of the boiling point and for the virial coefficients is presented. Values for L are calculated from the experimental L_a -values, using one of the derived p-T relations for the evaluation of V_G .

The values of the triple point temperature fitting to the mentioned p-T relations are derived from the measured triple point pressure. In the third chapter the results of the measurements and the calculations are also compared with results of other authors and with other p-T relations.

In chapter IV the results of the measurements of the apparent heat of vaporization of ^4He are presented.

The calculation of the true heat of vaporization and the molar volume of the saturated vapour of helium from the apparent heat of vaporization are also discussed in chapter IV.

The results for L and V_G are compared with data of other authors and with results obtained from other thermodynamic calculations.

CHAPTER II

EXPERIMENTAL EQUIPMENT

The experimental equipment consists of four parts: the calorimeter assembly, the manometer system to measure and regulate the pressure in the calorimeter, the equipment to measure the amount of vapour liberated from the calorimeter and the equipment to measure the energy supply.

The calorimeter assembly is shown in fig. 1. The inner volume of the copper reservoir A is about 11 cm^3 . This reservoir is suspended from the bottom of a copper block B by means of a pressure tube and a flow tube, both of stainless steel and with inner diameters of 1.5 mm, and outer diameters of 2 mm. The copper block B is suspended from the cap of the cryostat by means of a vacuum tube of stainless steel.

The distance from the cap of the cryostat to the top of the copper block B is about 80 cm. From the top of the copper block B up to 20 cm below the cap of the cryostat the flow tube has an inner diameter of 2 mm and the pressure tube of 1.5 mm, the outer diameters being 2.5 and 2 mm respectively.

The connection between the capillaries below and above the copper block is formed by two bores in this block with diameters of 3 mm. At this place the gas in the flow and pressure tubes is in good thermal contact with the copper block B and therefore with the surrounding bath.

The upper parts of the flow and pressure tubes have inner diameters of 3 and 2 mm respectively. In the copper block B there are also a bore to connect the vacuum tube above the block with the vacuum jacket beneath it, and a cavity to be used as the reservoir of a vapour pressure thermometer. The diameters of the bore and the cavity are both 6 mm. From the top of the copper block B up to 10 cm above the cap of the cryostat the flow and the pressure tube of the calorimeter and the capillary of the vapour pressure thermometer are surrounded by the vacuum tube.

The inner diameter of the capillary of the vapour pressure thermometer is 1.5 mm up to 20 cm below the cap of the cryostat and it is 2 mm further upwards; the outer diameters are 2 and 2.5 mm respectively.

The electrical heater consists of a manganin wire with a diameter of 0.1 mm and a length of about 150 cm wound around four copper tubes with diameters of 5 mm and lengths of 10 mm. These tubes are soldered to the bottom of the reservoir A. The walls of the tubes are perforated to connect the liquid inside and outside the tubes. The resistance of the heating coil can be represented by $R = \{108.81 + 0.077 (T-20)\} \Omega$ in the temperature range from 13.5 °K to 24°K and by $R = \{107.70 + 0.037 (T-4.25)\} \Omega$ in the temperature range from 2.2 °K to 5°K.

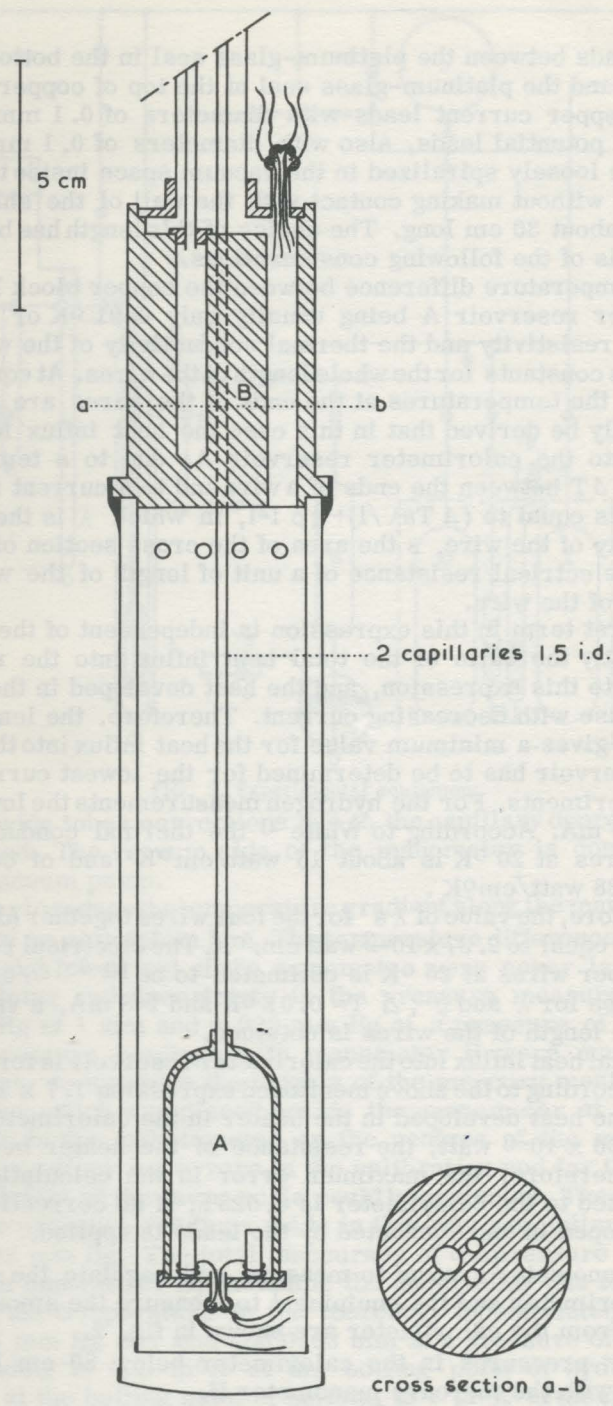


FIG. 1. Calorimeter

The leads between the platinum-glass seal in the bottom of reservoir A and the platinum-glass seal at the top of copper block B are two copper current leads with diameters of 0.1 mm and two constantan potential leads, also with diameters of 0.1 mm. These leads were loosely spiralized in the vacuum space inside the radiation shield without making contact with the wall of the shield. The leads are about 30 cm long. The choice of this length has been made on the basis of the following considerations.

The temperature difference between the copper block B and the calorimeter reservoir A being usually only 0.01 °K or less, the electrical resistivity and the thermal conductivity of the wires can be taken as constants for the whole length of the wires. At equilibrium conditions the temperatures at the ends of the wires are constant. It can easily be derived that in this case the heat influx for a unit of time into the calorimeter reservoir A, due to a temperature difference ΔT between the ends of a wire and to a current i through the wire, is equal to $(\Delta T s \lambda / l) + \frac{1}{2} \rho i^2 l$, in which λ is the thermal conductivity of the wire, s the area of the cross section of the wire and ρ the electrical resistance of a unit of length of the wire. l is the length of the wire.

The first term in this expression is independent of the current. Consequently the ratio of the total heat influx into the reservoir according to this expression, and the heat developed in the heater, will increase with decreasing current. Therefore, the length of the wires that gives a minimum value for the heat influx into the calorimeter reservoir has to be determined for the lowest current used in the experiments. For the hydrogen measurements the lowest current was 8 mA. According to White ¹⁾ the thermal conductivity of copper wires at 20 °K is about 15 watt/cm°K and of constantan wires 0.088 watt/cm°K.

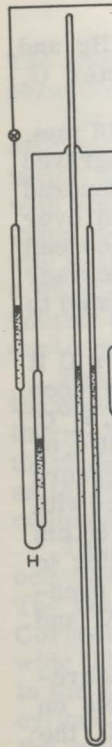
Therefore, the value of λs for the four wires together (diameters 0.1 mm) is equal to 2.37×10^{-3} watt cm/°K. The electrical resistance of the copper wires at 20 °K is estimated to be 10^{-3} Ω/cm. Using these values for λ and ρ , $\Delta T = 0.01$ °K and $i = 8$ mA, a value of 28 cm for the length of the wires is obtained.

The total heat influx into the calorimeter reservoir is for a current of 8 mA according to the above mentioned expression 1.7×10^{-6} watt, whereas the heat developed in the heater in the calorimeter reservoir is 6900×10^{-6} watt, the resistance of the heater being about 108Ω . Therefore, the maximum error in the calculation of the heat supplied to the calorimeter is 0.025%, if no correction for the heat developed in and conducted by the leads is applied.

The manometer system to measure and regulate the pressure in the calorimeter and the equipment to measure the amount of gas liberated from the calorimeter are shown in fig. 2.

Vapour pressures in the calorimeter below 80 cm Hg were measured with the mercury manometer H.

The inner diameters of the tubes of this manometer are 20 mm.



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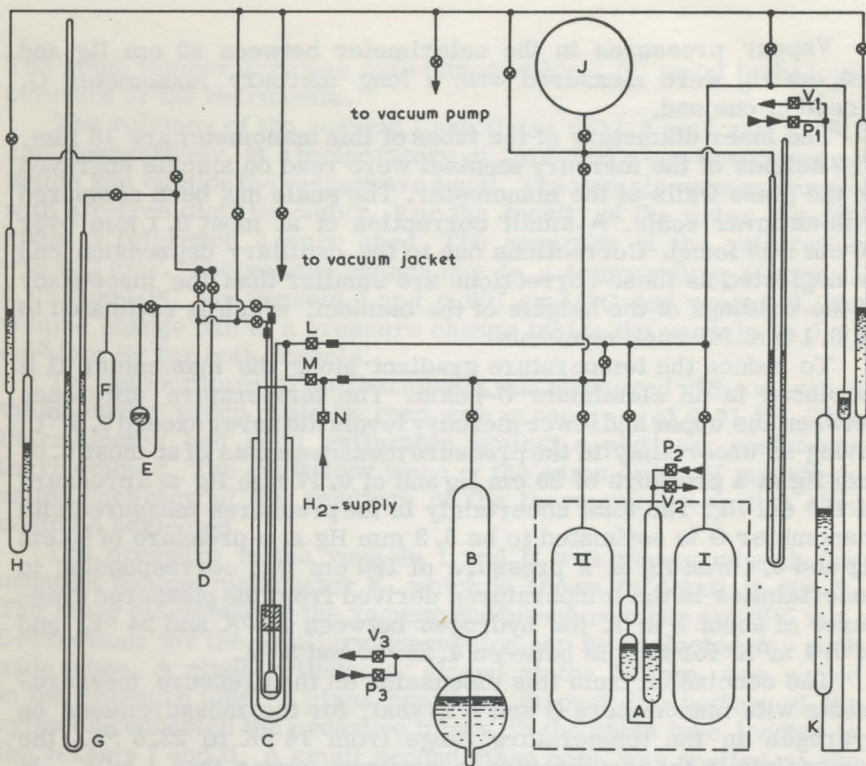


FIG. 2. Experimental equipment

For such wide tubes corrections due to the capillary depression can be neglected. The vacuum side of the manometer is connected to the high vacuum pump.

In order to reduce the temperature gradient along the manometer it is placed in an aluminium box. The temperature differences between the upper and lower end of the manometer were never larger than 0.3°C , giving an uncertainty in the pressure measurements of 0.04 mm Hg at 1 atm and 0.003 mm Hg at a pressure of 5 cm Hg .

The pressure readings with manometer H were made with a cathetometer to measure the heights of the mercury menisci on an invar scale, which was placed beside the manometer at the same distance from the cathetometer as the centres of the manometer tubes. Corrections for errors in the calibration and for the expansion coefficient of the invar scale could be neglected. The inaccuracies of the pressure readings made in this way are estimated to be within 0.02 mm Hg . The total inaccuracy of the pressure measurements with manometer H, including the uncertainty due to inhomogeneity of the temperature in the mercury, is estimated to be at most 0.06 mm Hg at 1 atm and 0.03 mm at a pressure of 5 cm Hg , corresponding to $0.3\text{ m}^{\circ}\text{K}$ at the boiling point of hydrogen, to $0.1\text{ m}^{\circ}\text{K}$ at the boiling point of helium, to $1\text{ m}^{\circ}\text{K}$ at the triple point of hydrogen and to $0.3\text{ m}^{\circ}\text{K}$ for helium at 2.2°K .

Vapour pressures in the calorimeter between 80 cm Hg and 180 cm Hg were measured with a long mercury manometer G, closed at one end.

The inner diameters of the tubes of this manometer are 16 mm. The heights of the mercury menisci were read on a scale engraved on the glass walls of the manometer. The scale has been compared with an invar scale. A small correction of at most 0.1 mm over 60 cm was found. Corrections due to the capillary depression can be neglected as these corrections are smaller than the inaccuracy of the readings of the heights of the menisci, which is estimated to be 0.1 mm for each meniscus.

To reduce the temperature gradient along the manometer G it is placed in an aluminium U-beam. The temperature difference between the upper and lower mercury levels did never exceed 0.5°C , giving an uncertainty in the pressure measurements of at most 0.07 mm Hg at a pressure of 80 cm Hg and of 0.17 mm Hg at a pressure of 180 cm Hg. The total uncertainty in the pressures measured with manometer G is estimated to be 0.3 mm Hg at a pressure of 80 cm Hg and 0.4 mm Hg at a pressure of 180 cm Hg, corresponding to uncertainties in the temperatures derived from the measured pressures of about $1\text{ m}^{\circ}\text{K}$ for hydrogen between 21°K and 24°K , and of $0.4\text{ m}^{\circ}\text{K}$ for helium between 4.25°K and 5°K .

The conclusion from this discussion on the pressure measurements with manometers G and H is that, for the measurements on hydrogen in the temperature range from 14°K to 23.5°K , the uncertainty in the temperature is nowhere larger than $1\text{ m}^{\circ}\text{K}$. In this temperature range the largest value of the derivative of the apparent heat of vaporization with respect to the temperature is about $12\text{ J/mole}^{\circ}\text{K}$ at 23.5°K . Therefore the uncertainty of $1\text{ m}^{\circ}\text{K}$ in the temperature gives an uncertainty in L_a of at most 0.012 J/mole , which is 0.001% of the value of L_a at 23.5°K .

For the measurements on helium in the temperature range from 2.2°K to 5°K the uncertainty in the temperature is nowhere larger than $0.4\text{ m}^{\circ}\text{K}$. The largest value of dL_a/dT for helium below 4.5°K is $14\text{ j/mole}^{\circ}\text{K}$ at 4.5°K , and dL_a/dT increases between 4.5°K and 5°K to $60\text{ J/mole}^{\circ}\text{K}$ at 5°K . Therefore, the uncertainty of $0.4\text{ m}^{\circ}\text{K}$ in the temperature gives an uncertainty in L_a of at most 0.006 J/mole below 4.5°K , which is about 0.006% of the value of L_a at 4.5°K , whereas between 4.5°K and 5°K the uncertainty increases to 0.024 J/mole at 5°K , which is about 0.03% of the value of L_a at 5°K .

The constancy of the pressure in the calorimeter reservoir A was checked with the oil manometer E. The vessel F was immersed in ice in order to keep the reference pressure for manometer E constant. The temperature difference between the copper block B and the calorimeter reservoir A was measured with the differential oil manometer D.

The evaporated gas was gathered in the calibrated vessels I and II, which are placed in a thermostat, filled with water. The temperature in the thermostat can be kept constant within $\pm 0.01^{\circ}\text{C}$.

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The room temperature was maintained within 1 °C equal to the temperature of the thermostat.

The volumes of the vessels I and II are 8232.2 cm³ and 8779.3 cm³ respectively, at a temperature of 20°C and when the pressures inside and outside the vessels are equal. The vessels were calibrated with air-free distilled water. For the density of the water the data given in reference 2 were used. The accuracy of the calibration was 0.2 cm³. The volume change due to a temperature change is 0.091 cm³/°C for vessels I and 0.097 cm³/°C for vessel II. The volume change due to a pressure change inside the vessels is 0.01 cm³/cm Hg for both vessels.

The temperature in the thermostat was measured with a mercury thermometer which could be read with an accuracy of 0.01 °C. This thermometer had been calibrated against a platinum resistance thermometer. The deviations were of the same order of magnitude as the accuracy of the readings of the thermometer so that they could be neglected.

The pressure in the vessels I and II was measured with the constant volume manometer K, which is shown in detail in fig. 3. The inner diameters of the vacuum and pressure tubes are 26.5 mm. Corrections for the capillary depression can be neglected for such wide tubes. A glass cylinder a, closed at the bottom, was waxed in the pressure tube. A glass capillary through the bottom of the cylinder connected the pressure tube with the glass tube leading to the vessels I and II. A small ground glass cone was melted at the centre of the bottom of the cylinder. This cone was illuminated from above by means of a glass prism placed on the top of the cylinder.

The vacuum and pressure tubes of the manometer were connected with each other and with the mercury reservoir b by glass capillaries with inner diameters of 3 mm. Before the mercury flows from the reservoir into the manometer it has to pass through an air trap c, which reduces the possibility that air, which may be in the mercury, enters into the manometer. The level in the pressure tube can be adjusted, so that it touches the glass cone, by means of the needle valves P₁ and V₁ (see fig. 2) by which the pressure above the mercury level in the reservoir b can be regulated. The manometer and reservoir are placed in an aluminium box in order to reduce the temperature gradient along the manometer.

The dead volume between the mercury level in the constant volume manometer, the vessels I and II and the needle valves L and M was determined by gas pressure measurements using the calibrated small vessels A with volumes of 50 and 100 cm³, placed in the thermostat. The mercury level in the vessels A could be changed by means of the needle valves P₂ and V₂, connected with a pressure line and a vacuum line respectively. The total dead volume is 164.0 cm³, if vessel II is connected with the constant volume manometer, and 79.7 cm³ if vessel I is connected with the manometer. The accuracy of the calibration of the dead volume is 0.2 cm³.

The amount of gas, liberated from the calorimeter was calculated

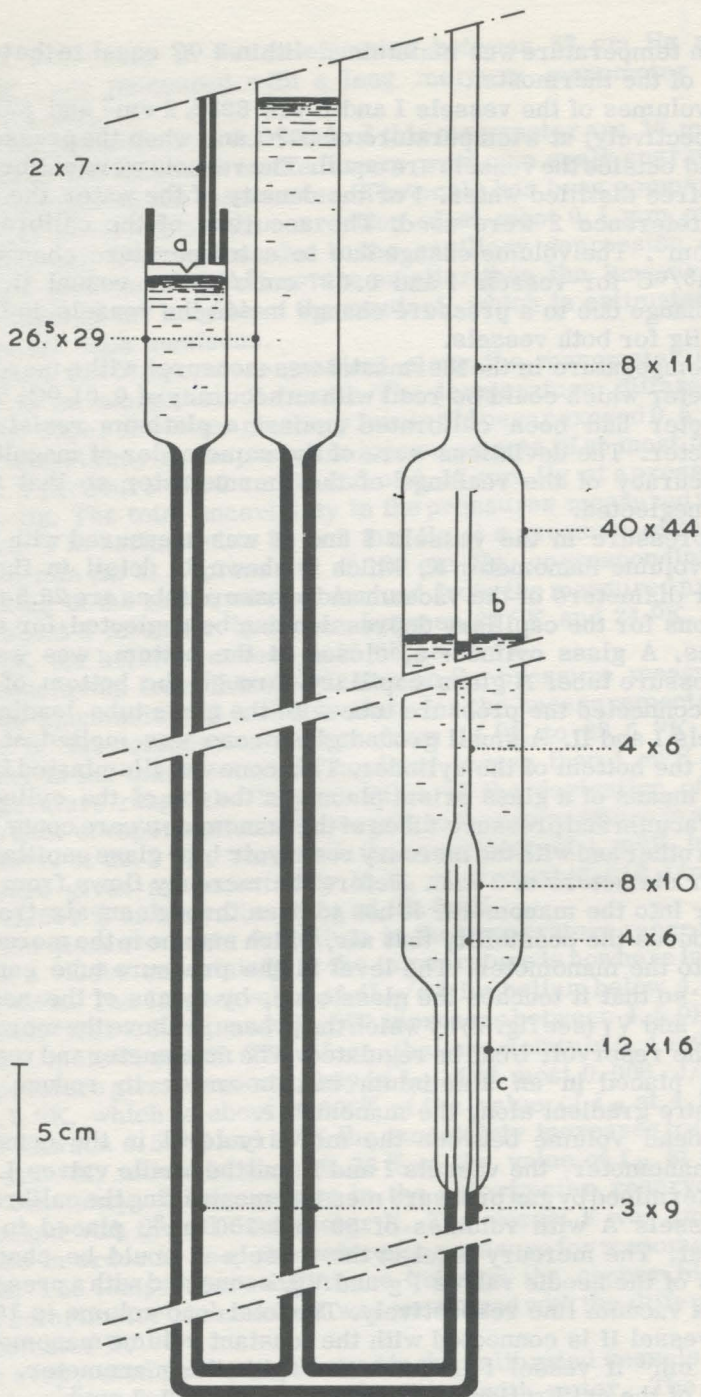


FIG. 3. Constant volume manometer

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from the pressure, volume and temperature of the gas in the vessels I and II, with the equation $n(1 + nB/V) = pV/RT$, where n is the number of moles of gas and V the volume of the vessels. For the gas constant R a value of $8.31432 \text{ J/mole}^\circ\text{K}$ was used. As n was never larger than 0.08 mole in a volume of 8000 cm^3 and B at room temperature is about $14 \text{ cm}^3/\text{mole}$ for hydrogen and $11 \text{ m}^3/\text{mole}$ for helium, the approximate value pV/RT can be taken for n in the correction term. Further approximation is not necessary. The influence of the third virial coefficient can be neglected.

The hydrogen or helium gas was condensed into the calorimeter by means of the compressor B. The volume of B is about 2000 cm^3 .

The heat input was calculated from the heating current, the resistance of the heater and the time. The heating current was determined by measuring the voltage across a standard resistance of 10Ω in series with the heater, by means of a Diesselhorst potentiometer.

The resistance of the heater was measured as a function of temperature and was checked in every experiment by comparing it with the standard resistance. The inaccuracies in the calibrations of the standard resistance and of the standard cell used for the adjustment of the current through the Diesselhorst potentiometer could be neglected. The accuracy of the measurements of the resistance of the heater and of the voltage across the standard resistance is 0.005% .

The time measurements were made with two stopwatches which could be read with an accuracy of 0.01 s . They were compared with each other and with the standard time signal of the "American Forces Network" radio station in Germany. From the scattering of the comparison data the accuracy of the time measurements with these watches is estimated to be 0.01% of the measured time, which varied from 15 minutes to 3 hours.

The experimental procedure was as follows. The vacuum jacket of the calorimeter assembly was evacuated at nitrogen temperature before the measurements on hydrogen, or at hydrogen temperature before the measurements on helium. After closing of the stopcock which connects the vacuum jacket to the high vacuum pump, the apparatus was cooled down to hydrogen or helium temperature.

About 8.5 cm^3 liquid was then condensed in the calorimeter reservoir A and about 0.5 cm^3 in the vapour pressure thermometer in the copper block B. After the adjustment of the temperature in the cryostat at the desired value, the evaporation was started by switching on the heating current.

Initially the pressure in the calorimeter was regulated by means of the needle valve M, the evaporated gas being pumped off via the dead volume of vessel II. Between the copper block B and the calorimeter a temperature difference of about $0.01 \text{ }^\circ\text{K}$ was established, the temperature in the copper block being higher in order to prevent condensation in the capillaries at this place.

The total time of the evaporation was divided into three periods:

the foreperiod during which the evaporated gas was pumped off, the first measuring-period during which the gas was gathered in vessel I and the second measuring-period during which the gas was gathered in vessel II. At the end of the foreperiod the valve M was closed and simultaneously a stopwatch was started. Then, immediately, valve L to vessel I was opened. At the end of the first measuring-period valve L was closed and simultaneously the first watch was stopped and the second one was started. Then, immediately, valve M to vessel II was opened. At the end of the second measuring-period valve M was closed and simultaneously the second watch was stopped. The time difference between closing a valve and stopping or starting a stopwatch is estimated to be $+ 0.3$ s.

The length of the measuring-periods varied from 20 to 75 minutes. It appeared that the length of the foreperiod should be larger than a minimum value, which depends on the pressure in the calorimeter. The main difficulty in these experiments is namely, that after the onset of the evaporation the temperature in the capillaries decreases and hence the amount of gas in these capillaries increases, the pressure being kept constant. To a first approximation it follows from $pV = nRT$ that $\Delta n = -pV \Delta T / RT^2$, where n is the number of moles of gas in the capillaries. Therefore, the influence of a certain temperature change on the amount of gas in the capillaries is larger at high pressures than at low pressures.

As Δn is inversely proportional to the square of the temperature in the capillaries, the influence of a certain temperature change is larger for helium than for hydrogen.

The division of the measuring-period into two parts made it possible to decide whether the foreperiod had been taken long enough to reach sufficient equilibrium. If not, the result for L_a from the first measuring-period was higher than that from the second one.

Extreme care was taken to make the pressure in the calorimeter at the end of a measuring-period within 0.5 mm oil equal to the pressure at the beginning of the period. In this way corrections for pressure and temperature changes in the calorimeter were avoided.

For most temperatures at which L_a was measured, the measurements of L_a were repeated once or twice with a different heating current in order to check the influence of the heat leak. Within the accuracy of the measurements the results for L_a did not depend on the heating current. The heat leak was also checked before starting the evaporation by reducing the temperature in the calorimeter by means of the valve M a few hundredths of a degree below the temperature of the copperblock B and then closing that valve. Only when the heat leak was found to be negligibly small the experiment was continued.

When the experiments with this apparatus were started, the potential and current leads of the heater had been led from the calorimeter reservoir to the top of the cryostat through the flow capillary. The measurements made with the apparatus in this form at the boiling point of hydrogen showed very clearly the temperature decrease in

the capillaries. After the onset of the evaporation the resistance of the current leads decreased rather rapidly. Measurements of the resistance of the current leads as a function of time made it possible to determine the time after which the temperature change in the capillaries during the measuring-periods would be small enough to give only negligible errors in the results for L_a . The measurements at the boiling point of hydrogen showed that after half an hour these conditions had been achieved. Unfortunately, the results of these measurements were mostly 0.5 to 1% too low, indicating a heat leak, which was probably due to a bad thermal contact of the wires in the flow capillary with the copper block B. After modifying the apparatus into the form described in the beginning of this chapter, reproducible results were obtained.

CHAPTER III

THE HEAT OF VAPORIZATION AND THE TRIPLE POINT PRESSURE OF 20.4 °K-EQUILIBRIUM HYDROGEN

1. Introduction

When normal hydrogen, which is a mixture of 75 % ortho and 25 % para hydrogen is liquefied in contact with a suitable catalyst, the composition of the liquid mixture changes until the equilibrium condition is achieved. At 20.4 °K the equilibrium composition is 0.21 % ortho and 99.79 % para hydrogen. As the vapour pressure of the liquid mixture depends on the composition, it is very important to know the composition of the hydrogen in the case of measuring the vapour pressure to derive the temperature from it.

Because of the slow conversion of liquid normal hydrogen in a vapour pressure thermometer into equilibrium hydrogen, equilibrium hydrogen rather than normal hydrogen is preferred for establishing an accurate p-T relation which can be used for temperature measurements in the liquid hydrogen temperature range.

For the derivation of an accurate p-T relation for equilibrium hydrogen, using equation (2) of chapter I, very accurate values for the apparent heat of vaporization L_a as a function of temperature are needed. The available data of L_a are insufficiently accurate. Simon and Lange ³⁾ measured the heat of vaporization of, probably, about normal hydrogen. They represented their results by the equation

$$L = 219.7 - 0.27 (T-16.6)^2, \quad (1)$$

where L is expressed in cal/mole. Assuming that these experiments were made on normal hydrogen, and using the difference between the vapour pressures of normal and equilibrium hydrogen, Woolley, Scott and Brickwedde ⁴⁾ derived the following expression for the heat of vaporization of mixtures of ortho hydrogen and para hydrogen,

$$L = 217.0 - 0.27 (T-16.6)^2 + 1.4x + 2.9x^2 \quad (2)$$

where L is expressed in cal/mole. x is the mole fraction of ortho hydrogen. Equation (2) yields a value for L of 213.4 cal/mole for equilibrium hydrogen at its boiling point. Johnston, Clarke, Rifkin and Kerr ⁵⁾ measured the heat of vaporization of equilibrium hydrogen at the boiling point. They report a value of 214.8 ± 0.4 cal/mole.

These data are not accurate enough for the computation of an accurate p-T relation. In order to obtain more accurate data for the heat of vaporization of equilibrium hydrogen, the experiments described in this thesis were started.

Before the beginning of a series of measurements, normal hydrogen from the laboratory stock was converted into 20.4 °K-equilibrium hydrogen. The equilibrium hydrogen was stored in the vessels J, B and II (see fig. 2).

For the conversion of the normal hydrogen into equilibrium

hydrogen the method described by Durieux⁶⁾ was used. Fig. 4a shows a schematic diagram of the apparatus used for the conversion of the normal hydrogen into equilibrium hydrogen. The normal hydrogen was first passed through a copper spiral at 20.4 °K for purification and then it was condensed in a copper reservoir, also at 20.4 °K, filled with hydrous ferric oxide, with a height of 9 cm and a diameter of 1.4 cm. After waiting for a quarter of an hour the hydrogen was evaporated into the vessels with a speed of about 8 l gas of 1 atm and room temperature per hour. The vessels were filled with equilibrium hydrogen up to a pressure of about 80 cm Hg.

The composition of the converted hydrogen was determined by comparing its vapour pressure with that of freshly liquefied normal hydrogen and with that of converted hydrogen condensed in a reservoir containing a small amount of the catalyst. Fig. 4b shows a schematic diagram of the apparatus used for the determination of the composition of the converted hydrogen. To be sure that the normal hydrogen had indeed the high temperature equilibrium composition of 75% ortho and 25% para hydrogen, it was passed through a quartz capillary along a platinum wire, before it was condensed into the vapour pressure thermometer. The platinum wire was heated to a temperature of about 700 °C by means of an electric current. The para hydrogen concentration of the prepared converted hydrogen was always higher than 99 %.

According to Woolley e. a.⁴⁾ the theoretical value of the para hydrogen concentration in 20.4 °K-equilibrium hydrogen is 99.79 %.

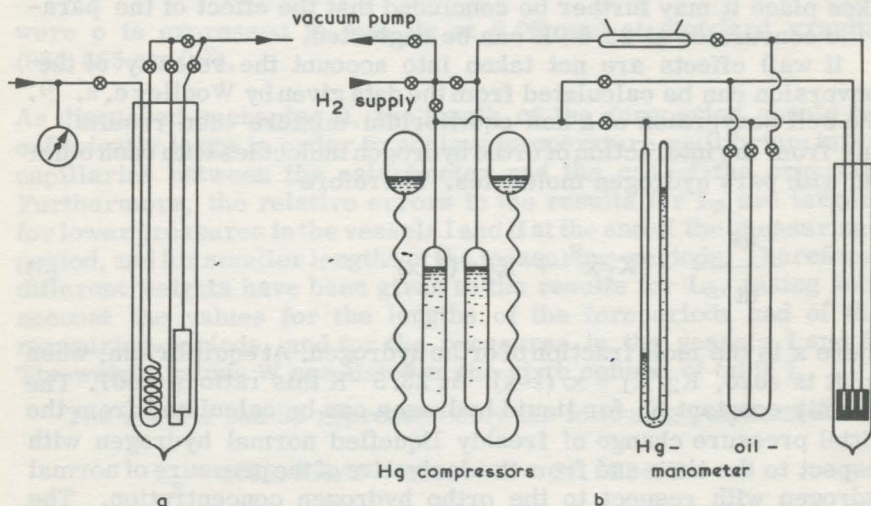


FIG. 4. a. Apparatus for the conversion of normal into equilibrium hydrogen.
b. Apparatus for checking the composition of the converted hydrogen.

Therefore, the inaccuracy in the composition of the hydrogen used for the measurements is at most 0.8 %. The derivative of the heat of vaporization of a mixture of ortho and para hydrogen with respect

to the mole fraction of ortho hydrogen, dL/dx , is according to equation (2), $(1.4 + 5.8x)$ cal/mole. When the mole fraction of ortho hydrogen is 1 %, dL/dx is equal to 1.46 cal/mole, so that the inaccuracy in the concentration of 0.8 % gives an uncertainty in L of 0.01 cal/mole. The value of L at 20.4 °K is about 215 cal/mole.

Therefore, the uncertainty in the para hydrogen concentration in the converted hydrogen of 0.8 % has only a negligible influence on the results for the heat of vaporization.

Several times the composition of the hydrogen, stored in vessel J, was checked about one week after the conversion at the end of a series of measurements. The para hydrogen concentration was found always to be still higher than 99 %.

When the temperature of 20.4 °K-equilibrium hydrogen is increased to e. g. 23.5 °K a slow conversion of 20.4 °K-equilibrium hydrogen into 23.5 °K-equilibrium hydrogen takes place. The ortho hydrogen concentration of 23.5 °K-equilibrium hydrogen is about 0.5 % higher than that of 20.4 °K-equilibrium hydrogen. As the para-ortho conversion is endothermic the effect of it would appear as a negative heat leak. When the heat leak was checked before the beginning of an evaporation experiment, it always was found to be negligibly small. Therefore it may be concluded that the negative heat leak due to the para-ortho conversion is of the same order of magnitude as the positive heat leak due to conduction along the capillaries and the potential and current leads. From the fact that the heat leak was also negligibly small at 20.4 °K, where no conversion takes place it may further be concluded that the effect of the para-ortho conversion at 23.5 °K can be neglected.

If wall effects are not taken into account the velocity of the conversion can be calculated from the data given by Woolley e. a. ⁴⁾. The self conversion of a non-equilibrium mixture then results only from the interaction of ortho hydrogen molecules with each other and with para hydrogen molecules. Therefore

$$\frac{dx}{dt} = -K_1 x^2 + K_2 x(1-x) \quad (3)$$

where x is the mole fraction of ortho hydrogen. At equilibrium, when dx/dt is zero, $K_2/K_1 = x/(1-x)$. At 23.5 °K this ratio is 0.007. The velocity constant K_1 for liquid hydrogen can be calculated from the initial pressure change of freshly liquefied normal hydrogen with respect to the time and from the derivative of the pressure of normal hydrogen with respect to the ortho hydrogen concentration. The values given by Woolley e. a. are $dp/dt = 0.23$ mm per hour and $dp/dx = 36$ mm, from which follows that $dx/dt = 0.0064$ /hour.

For normal hydrogen x is equal to 0.75. Substitution of these values for dx/dt , and K_2/K_1 in equation (3) gives a value for K_1 of 0.0114 per hour.

The concentration of ortho hydrogen in 20.4 °K-equilibrium hydrogen is 0.0021 for which equation (3) yields a value for dx/dt of 2×10^{-7} /hour. Therefore when the temperature of 20.4 °K-equilibrium hydrogen is increased to 23.5 °K, the initial velocity of the para-ortho conversion will be only 2×10^{-5} % per hour, when wall effects and the effects of impurities are neglected.

2. Experimental results for L_a

The values for the apparent heat of vaporization L_a , obtained from the measurements on 20.4 °K-equilibrium hydrogen are listed in table I. In this table are also given the pressure p , the temperature T , the amount of heat supplied to the calorimeter and the length of the measuring-period t .

During the measurements the current decreased slowly, probably due to a decrease of the EMF of the battery after switching on the current. Therefore, the heat supply to the calorimeter was determined by graphical integration of i^2 from a graph giving i^2 versus the time. The inaccuracy in the measurements of i was 0.005 % or less. The L_a -value at 20.4 °K is a mean value obtained from several measurements with the apparatus described at the end of chapter II. The temperatures are derived from the measured pressures using the vapour pressure-temperature relation T_{L60} for equilibrium hydrogen, calculated by Durieux ⁶⁾ ⁷⁾, and defined by the equation

$$10 \log p = 4.635384 - 44.2674/T + 0.021669T - 0.000021 T^2 \quad (4)$$

where p is expressed in mm Hg at 0 °C and at standard gravity (980.665 cm/s^2).

As discussed in chapter II, the length of the foreperiod should be sufficiently large in order to achieve temperature equilibrium in the capillaries between the calorimeter and the cap of the cryostat. Furthermore, the relative errors in the results for L_a are larger for lower pressures in the vessels I and II at the end of the measuring-period, and for smaller lengths of the measuring-periods. Therefore, different weights have been given to the results for L_a , taking into account the values for the lengths of the foreperiods and of the measuring-periods, and for the pressures in the vessels I and II. The weight values W are listed in the sixth column of table I.

The results can be represented by the following polynomial:

$$L_a = 1705.950/T + 423.1113 + 35.67347T + \\ - 0.520294T^2 - 0.0119735T^3 \quad (5)$$

which has been fitted to the experimental data by a least squares procedure and where L_a is expressed in J/mole. In fig. 5, L_a according to equation (5) is given as a function of T . In fig. 6, the deviations of the experimental values from this curve are shown.

TABLE I

Experimental results for L_a of $e-H_2$						
P mmHg 0°C	T _{L60} °K	time s	i^2Rt joule	$10^3 n_a$ mole	L_a joule mole	W
56.91	13.930	1201.6	20.583	22.651	908.7	$\frac{1}{2}$
56.91	13.930	1202.0	20.575	22.620	909.6	1
57.50	13.948	1801.7	19.547	21.516	908.5	$\frac{1}{2}$
57.50	13.948	1801.6	19.532	21.479	909.4	1
57.87	13.959	3001.1	20.795	22.867	909.4	1
57.87	13.959	3000.2	20.771	22.834	909.6	1
78.85	14.520	2717.6	29.452	32.301	911.8	1
78.85	14.520	2702.3	29.266	32.079	912.3	2
80.12	14.550	1805.1	30.481	33.422	912.0	1
80.12	14.550	1802.8	30.428	33.349	912.4	2
111.94	15.207	2401.0	41.148	44.945	915.5	$\frac{1}{2}$
111.94	15.207	2401.6	41.115	44.874	916.2	1
160.57	15.978	3610.1	61.560	67.034	918.3	1
160.57	15.978	3607.9	61.465	66.988	917.6	1
162.31	16.002	2415.9	59.542	64.850	918.2	1
162.31	16.002	2407.4	59.272	64.570	918.0	2
223.77	16.751	2701.7	66.540	72.288	920.5	$\frac{1}{2}$
223.77	16.751	2700.6	66.436	72.149	920.8	1
299.01	17.483	3604.2	61.855	67.118	921.6	1
299.01	17.483	3602.2	61.754	67.039	921.2	2
304.12	17.527	2703.3	66.691	72.411	921.0	1
304.12	17.527	2724.3	67.162	72.883	921.5	2
396.96	18.254	2701.5	66.644	72.307	921.7	1
396.96	18.254	2702.8	66.607	72.258	921.8	2
505.76	18.961	2717.2	67.111	72.855	921.2	2
505.76	18.961	2702.1	66.681	72.398	921.0	2
512.34	19.000	3608.4	61.855	67.218	920.2	1
512.34	19.000	3607.0	61.801	67.150	920.3	1
622.13	19.603	2700.6	66.743	72.644	918.8	1
622.13	19.603	2701.6	66.702	72.576	919.1	2
754.66	20.237	2704.9	66.760	72.761	917.5	1
754.66	20.237	2726.1	67.237	73.329	916.9	2
756.32	20.244	3602.2	61.937	67.517	917.4	1
756.32	20.244	3601.5	61.884	67.500	916.8	2
791.99	20.400	-	-	-	916.0	1
937.8	20.991	2702.2	66.759	73.095	913.3	2
1079.5	21.506	3621.0	62.304	68.499	909.6	1
1079.5	21.506	3604.9	62.051	68.147	910.6	1
1226.2	21.989	2700.8	66.840	73.756	906.2	2
1226.2	21.989	2701.1	66.814	73.761	905.8	1
1401.8	22.517	2100.2	51.984	57.668	901.5	2
1412.7	22.548	3602.0	62.010	68.785	901.5	2
1583.9	23.017	2701.5	66.957	74.620	897.3	1
1583.9	23.017	2704.0	66.993	74.714	896.7	2
1784.7	23.523	2705.6	67.086	75.235	891.7	1
1791.8	23.540	3609.9	62.101	69.710	890.9	2
1793.4	23.544	2715.9	67.264	75.559	890.2	2

The precision of the measurements can be estimated from fig. 6. The deviations are all within 0.08 %, whereas the standard deviation

$\Delta L_a = \sqrt{\sum \Delta_i^2 / (n-5)}$ is equal to 0.40 J/mole, when the same

weight is given to all experimental points. In this expression Δ_i is the deviation of the i th point, n is the number of experimental points and 5 is the number of coefficients of the polynomial. When the weights given to the experimental points according to table I are taken into account, the standard deviation is

$\Delta L_a = \sqrt{(\sum w_i \Delta_i^2) / \{(\sum w_i) - 5\}}$, which is equal to

0.35 J/mole.

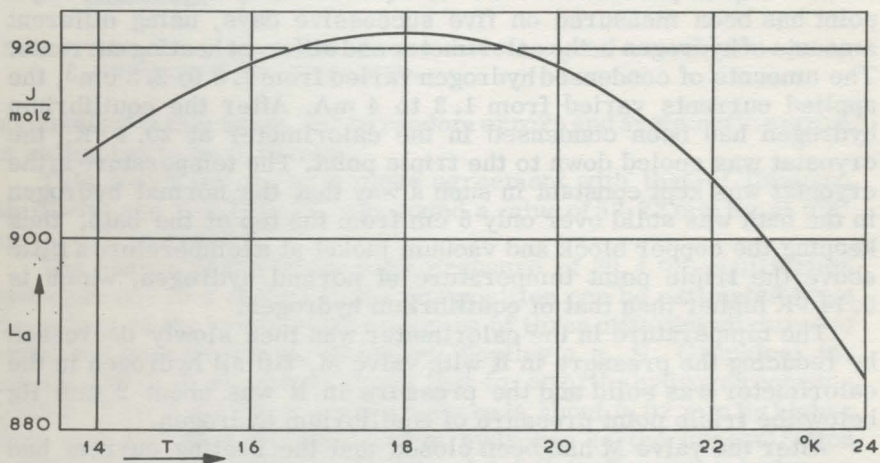


FIG. 5. The apparent heat of vaporization of e - H₂, L_a, versus T according to eq. (5).

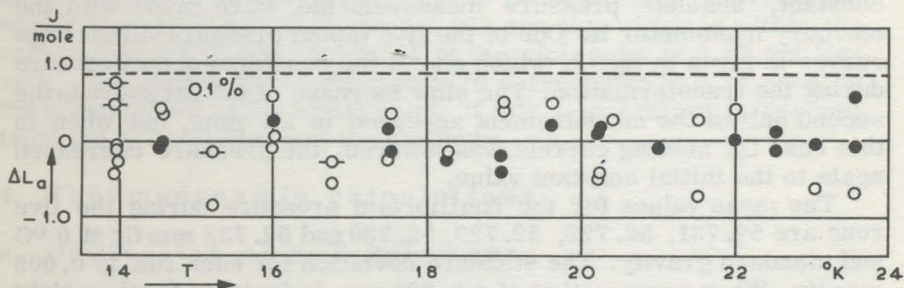


FIG. 6. Deviations of the experimental L_a-values from eq. (5).

$$\Delta L_a = L_a(\text{calc}) - L_a(\text{exp}).$$

- weight value $\frac{1}{2}$
- weight value 1
- weight value 2

Systematic errors may arise from the inaccuracies in the calibration of the vessels I and II, of the thermometer in the thermostat and of the stopwatches. These systematic errors are estimated to be together at most 0.02 %. The errors due to the uncertainties in the calibrations of the Diesselhorst potentiometer, of the standard resistance and of the standard cell used for adjusting the current through the potentiometer, could be neglected.

From the estimated precision and the estimated systematic errors the inaccuracy in the L_a -values, given by equation (5), is estimated to be at most 0.06 % if T is expressed on the T_{L60} scale.

3. The vapour pressure of equilibrium hydrogen at its triple point

The vapour pressure of 20.4 °K-equilibrium hydrogen at its triple point has been measured on five successive days, using different amounts of hydrogen in the calorimeter and different heating currents. The amounts of condensed hydrogen varied from 1.8 to 2.3 cm³, the applied currents varied from 1.3 to 4 mA. After the equilibrium hydrogen had been condensed in the calorimeter at 20.4 °K, the cryostat was cooled down to the triple point. The temperature in the cryostat was kept constant in such a way that the normal hydrogen in the bath was solid over only 5 cm from the top of the bath, thus keeping the copper block and vacuum jacket at a temperature a little above the triple point temperature of normal hydrogen, which is 0.14 °K higher than that of equilibrium hydrogen.

The temperature in the calorimeter was then slowly decreased by reducing the pressure in it with valve M, till all hydrogen in the calorimeter was solid and the pressure in it was about 2 mm Hg below the triple point pressure of equilibrium hydrogen.

After the valve M had been closed and the heating current had been switched on the increase of the pressure was first followed on the oil manometer E (see fig. 2) and, as soon as the pressure became constant, absolute pressure measurements were made with the mercury manometer H. One of the five vapour pressure versus time curves is given in fig. 7, which shows the constancy of the pressure during the transformation. The slow increase of the pressure in the second half of the measurement appeared in all runs, but when in this case the heating current was lowered, the pressure decreased again to the initial constant value.

The mean values for the equilibrium pressure during the five runs are 52.731, 52.728, 52.729, 52.730 and 52.732 mm Hg at 0 °C and standard gravity. The standard deviation for each run is 0.008 mm Hg. When a correction of + 0.002 mm is included for the weight of the hydrogen vapour in the capillary and - 0.001 mm Hg for the thermomolecular pressure difference, the result of the measurements of the vapour pressure of 20.4 °K-equilibrium hydrogen at its triple point, when the average is taken from the five mentioned values, is $p_{tr} = 52.731$ mm Hg at 0 °C and standard gravity. The

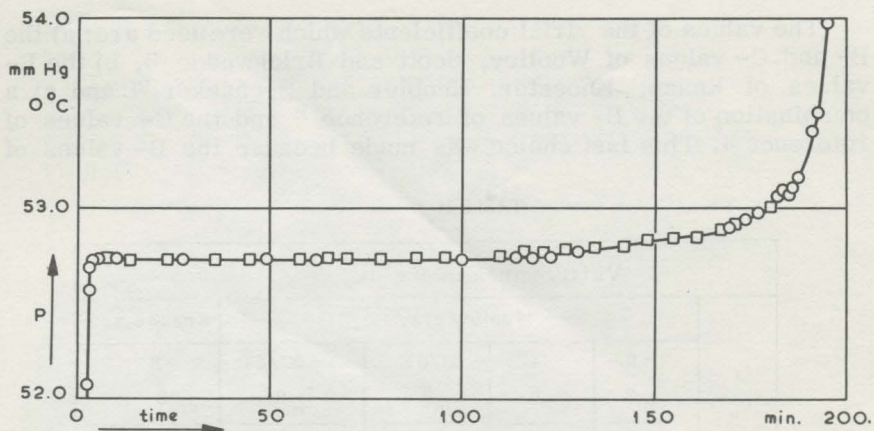


FIG. 7. The triple point pressure, p versus time showing the constancy of the pressure during one of the measurements.

uncertainty in this value, due to random errors and systematic errors, is estimated to be 0.01 mm.

This result for p_{tr} is in close agreement with that of Durieux, Muijlwijk and Van Dijk⁸⁾, who found a value of 52.73 mm Hg at 0°C and standard gravity.

The change of the triple point pressure of 20.4 °K-equilibrium hydrogen due to a change in the composition can be estimated from the values of the triple point pressure of three different mixtures of ortho and para hydrogen, given by Woolley *e. a.*⁴⁾. Graphical interpolation of these values shows that for an ortho hydrogen concentration of 10 % the triple point pressure is about 0.02 mm Hg higher than that for 20.4 °K-equilibrium hydrogen (ortho concentration 0.002). Therefore, the uncertainty of 0.8 % in the ortho hydrogen concentration of the hydrogen used for the measurements gives an uncertainty in the measured triple point pressure of 20.4 °K-equilibrium hydrogen of at most 0.002 mm Hg, which is within the accuracy of the result. As dp/dT at the triple point is 0.03 mm Hg/m°K, the uncertainty in the pressure corresponds to 0.07 m°K in the temperature of the triple point, if this temperature is derived from the p - T relation and the pressure.

4. Thermodynamic calculations

a. Derivation of p - T relations

Clapeyron's equation according to the formulation of eq. (2), chapter I, was used to derive four different vapour pressure-temperature relations for 20.4 °K-equilibrium hydrogen. The difference between these p - T relations is due to the use of different values of the virial coefficients B and C and to the choice of the temperature of the normal boiling point.

The values of the virial coefficients which were used are: a) the B- and C- values of Woolley, Scott and Brickwedde ⁴), b) the B-values of Knaap, Knoester, Knobler and Beenakker ⁹) and c) a combination of the B- values of reference 9 and the C- values of reference 4. This last choice was made because the B- values of

TABLE II

Virial coefficients of e-H ₂					
T °K	Woolley e. a.				Knaap e. a.
	- B	C	dB/dT	-dC/dT	-B
	$\frac{\text{cm}^3}{\text{mole}}$	$\frac{\text{cm}^6}{\text{mole}^2}$	$\frac{\text{cm}^3}{\text{mole}^\circ\text{K}}$	$\frac{\text{cm}^6}{\text{mole}^2 \text{ }^\circ\text{K}}$	$\frac{\text{cm}^3}{\text{mole}}$
14	243.4	5398	24.50	571	250.5
15	220.8	4873	20.74	481	226.9
16	201.6	4430	17.76	409	207.3
17	185.2	4051	15.36	351	190.7
18	170.8	3724	13.40	304	176.0
19	158.2	3439	11.79	266	163.4
20	147.2	3190	10.45	234	152.5
21	137.3	2970	9.32	207	142.6
22	128.4	2775	8.36	184	133.8
23	120.6	2601	7.53	164	125.9
24	113.4	2446	6.82	147	118.9

Knaap e. a. were measured at relatively low pressures where the influence of C could be neglected, whereas in the calculations for the derivation of a p-T relation also higher pressures are needed. The B-values of reference 4 as well as those of reference 9 were corrected for the differences between the B-values of normal hydrogen and those of equilibrium hydrogen, measured by Beenakker, Varekamp and Knaap ¹⁰). The correction which was used is $B_n - B_e = (6.22 - 0.23T) \text{ cm}^3/\text{mole}$. The temperature dependence is somewhat arbitrary because of the uncertainty in the data. The values of B and C, which were used for the calculations, are given in table II for every °K. The values for every 0.1 °K were obtained by graphical interpolation.

For each of the three sets of virial coefficients the derivation of a p-T relation was performed with a value of 20.267 °K for the temperature of the normal boiling point, which value has been recommended by the Advisory Committee for Thermometry of the International Bureau of Weights and Measures (Paris, 1964). For the virial coefficients of Woolley e. a. the calculations were performed also with 20.260 °K, which is the temperature of the boiling point on the T_{L60} scale.

As a first approximation V_G was calculated at every 0.1 °K between 13.5 °K and 24 °K by iterative solution of the equation of state

$$p V_G = RT (1 + B/V_G + C/V_G^2),$$

using the T_{L60} scale for the relation between the pressure of the saturated vapour, p , and T . With these values of V_G and with L_a according to eq. (5), in which T is expressed on the T_{L60} scale, $d \ln p/dT$ was evaluated at every 0.1 °K. By a least squares procedure a polynomial of the form

$$d \ln p/dT = \sum_{n=-2}^{+2} a_n T^n$$

was fitted through these values of $d \ln p/dT$.

By integrating this expression, using the temperature of the boiling point as a fixed point, a first approximation of the p - T relation was obtained. With this first approximation the calculation of V_G , $d \ln p/dT$ and the p - T relation was repeated to obtain a second approximation of the p - T relation. Then the temperatures for the experimental L_a -values were derived from the measured pressures according to this second approximation of the p - T relation and a new equation for $L_a(T)$ was computed. These new L_a -values and the second approximation of the p - T relation were used to calculate V_G , $d \ln p/dT$ and the third approximation of the p - T relation.

As the maximum difference between the third approximation and the second one was only a few tenths of a millidegree, no further approximation was necessary. The calculations with the virial coefficients of Woolley *et al.* and a value of 20.267 °K for the temperature of the normal boiling point resulted in the p - T relation:

$$\ln p = 18.87461 - 118.9599/T - 4.06773 \ln T + 0.392698 T - 0.0061369 T^2 + 0.00005166 T^3, \quad (6)$$

where p is expressed in mm Hg at 0 °C and at standard gravity.

Table III gives the values of p according to eq. (6) and table IV the values of dp/dT for every 0.1 °K.

Similar relations were obtained from the three other calculations. In figure 8 the differences $\Delta T = T_X - T_{L60}$ for the four relations are shown. In figure 9 the p - T relation according to eq. (6) is compared with other p - T relations and the results of other authors. Fig. 9 shows that there is a rather good agreement between the derivative of the vapour pressure with respect to the temperature according to relation (6) (curve 1) and the derivative of the p - T relation of Hoge and Arnold¹¹⁾ (curve 2), who measured the vapour pressure of equilibrium hydrogen against a platinum resistance thermometer calibrated on the NBS-1939 scale. $d(T_1 - T_{L60})/dT - d(T_2 - T_{L60})/dT \ll 1.2 \times 10^{-3}$ between 14 and 24 °K.

Below the boiling point the difference between relation (6) and the p - T relation of Weber, Diller, Roder and Goodwin¹²⁾ (curve 3), which gives the vapour pressure of equilibrium hydrogen as a function

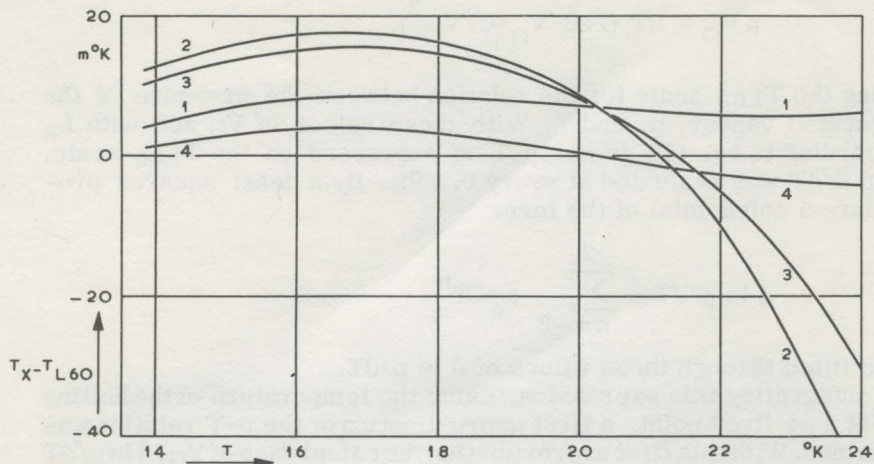


FIG. 8. Temperature differences $T_x - T_{L60}$, where x denotes the p - T relation calculated from L_a with the virial coefficients of

1. Woolley e. a.
2. Knaap e. a.
3. B of Knaap e. a. and C of Woolley e. a.
4. Woolley e. a., boiling point 20.260 °K.

} boiling point 20.267 °K.

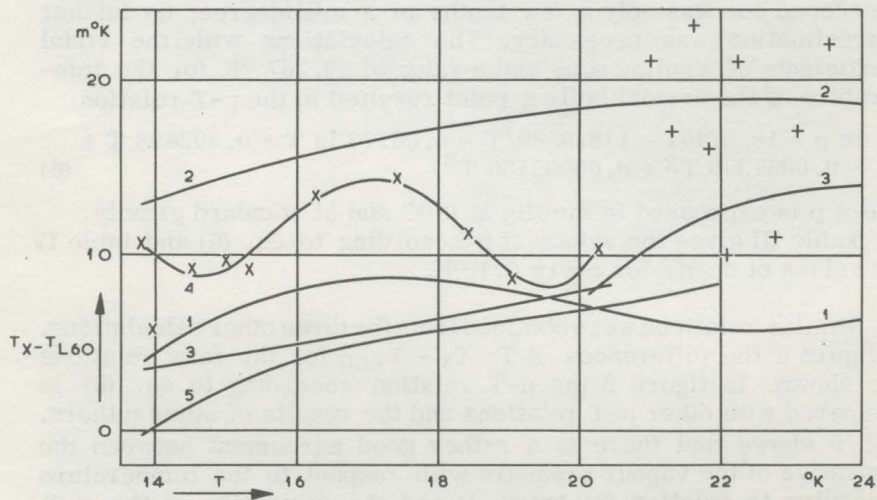


FIG. 9. Temperature differences $T_x - T_{L60}$, where x denotes the p - T relations:

1. Equation (6)
2. Hoge e. a. (T_2 on the NBS - 1939 scale)
3. Weber e. a. (T_3 on the NBS - 1955 scale)
4. Barber e. a. (T_4 on the NPL scale, x experimental values)
5. Van Rijn e. a. (T_5 from magnetic temperature measurements, using 20.267 °K as a reference point)

+ Experimental results of Van Itterbeek e. a. (T on the NPL scale).

of the temperature on the NBS-1955 scale, is less than 3 m°K. The p-T relation of Weber e. a. below the boiling point is based on the data of Hoge and Arnold expressed on the NBS-1955 scale. The measurements of Barber and Horsford ¹³⁾ (curve 4) on the NPL scale agree with relation (6) within 6 m°K.

Above 22 °K the p-T relation of Weber e. a. ¹²⁾, derived from measurements with platinum resistance thermometers calibrated on the NBS-1955 scale, and the measurements of Van Itterbeek, Verbeke, Theewes, Staes and De Boelpaep ¹⁴⁾, who used a platinum resistance thermometer calibrated on the NPL scale, are about 10 m°K higher than relation (6).

The magnetic temperature measurements given in references 6 and 7, which were used in the derivation of the T_{L60} scale, are within the accuracy of the results in agreement with this scale. The T_{L60} scale has above 17 °K about the same slope as relation (6). Provisional results of magnetic temperature measurements on manganese ammonium sulphate between the triple point of equilibrium hydrogen and 23 °K of Van Rijn, Durieux and Van Dijk ¹⁵⁾ confirm the T_{L60} scale, when taking 20.260 °K for the temperature of the boiling point. When 20.267 °K is chosen for the temperature of the boiling point, the results of Van Rijn e. a. ¹⁵⁾ (curve 5) agree with p-T relation (6) within the accuracy of the magnetic measurements and the data for L_a and the virial coefficients, used for the thermodynamic calculations.

None of these p-T relations and measurements confirm the behaviour of the curves 2 and 3 in fig. 8, which have been calculated from L_a with the B-values of Knaap e. a. Therefore, we prefer to take p-T relation (6) as the result from the measurements of L_a and the thermodynamic calculations.

The accuracy of p-T relation (6) depends on the accuracy of L_a and of the virial coefficients, when the boiling point is adopted as a fixed point. As discussed in section 2 of this chapter the estimated maximum error in L_a is ± 0.06 %. When Clapeyron's equation is integrated from the boiling point T_{B.P.} to a temperature T, an error of 0.06 % in L_a over this temperature range gives a maximum error of 0.06 % in T - T_{B.P.}. Consequently the maximum inaccuracy of p-T relation (6) due to the inaccuracy in L_a, will be between 3.6 m°K at 14 °K and 2.4 m°K at 24 °K.

The influence of the virial coefficients can be seen from fig. 8. Below 17 °K the slopes of the three p-T relations with 20.267 °K for the temperature of the boiling point are the same. Therefore, the differences between these relations are due to the differences between the values of the virial coefficients above 17 °K. Between 17 and 24 °K the B-values according to Woolley e. a. differ about 4 % from those according to Knaap e. a. The difference between the p-T relation calculated with the B-values of Woolley e. a. and the p-T relation calculated with the B-values of Knaap e. a., in both cases using the C-values of Woolley e. a., is -7 m°K at 14 °K and +36 m°K at 24 °K (see fig. 8, curve 1 and 3).

TABLE III

Vapour pressure of e-H ₂ , according to eq. (6). p in mm Hg, 0°C. g = 980.665 cm s ⁻²										
T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
14	59.098	62.526	66.106	69.841	73.737	77.796	82.025	86.427	91.007	95.770
15	100.721	105.863	111.204	116.746	122.495	128.455	134.633	141.032	147.658	154.516
16	161.611	168.948	176.532	184.369	192.463	200.820	209.446	218.345	227.523	236.986
17	246.737	256.785	267.132	277.786	288.751	300.033	311.637	323.569	335.835	348.441
18	361.391	374.691	388.347	402.365	416.750	431.508	446.645	462.166	478.078	494.385
19	511.093	528.209	545.737	563.685	582.057	600.859	620.097	639.777	659.905	680.486
20	701.527	723.033	745.009	767.463	790.399	813.823	837.742	862.161	887.087	912.524
21	938.478	964.957	991.965	1019.51	1047.59	1076.23	1105.41	1135.16	1165.47	1196.35
22	1227.80	1259.84	1292.47	1325.70	1359.52	1393.95	1428.99	1464.66	1500.94	1537.86
23	1575.41	1613.61	1652.45	1691.95	1732.11	1772.94	1814.44	1856.61	1899.48	1943.03
24	1987.28									

TABLE IV

$\frac{dp}{dT}$ of e-H ₂ , according to eq. (6), in mm Hg, 0°C/°K.										
T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
14	33.55	35.03	36.57	38.14	39.77	41.43	43.15	44.90	46.71	48.56
15	50.46	52.41	54.40	56.45	58.54	60.68	62.87	65.12	67.41	69.75
16	72.15	74.60	77.10	79.65	82.25	84.90	87.62	90.38	93.19	96.06
17	98.99	101.96	105.00	108.08	111.23	114.42	117.67	120.98	124.35	127.77
18	131.24	134.77	138.36	142.01	145.71	149.47	153.28	157.15	161.08	165.07
19	169.11	173.21	177.37	181.59	185.86	190.19	194.58	199.03	203.53	208.10
20	212.72	217.40	222.14	226.94	231.79	236.71	241.68	246.71	251.80	256.95
21	262.15	267.43	272.75	278.1	283.6	289.1	294.6	300.3	305.9	311.7
22	317.5	323.3	329.3	335.2	341.3	347.4	353.5	359.7	366.0	372.3
23	378.7	385.2	391.7	398.3	404.9	411.6	418.4	425.2	432.1	439.0
24	446.0									

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It may be concluded from the agreement, as shown in fig. 9, between the p-T relation (6) (curve 1), which is calculated with the B- and C- values of Woolley e. a., and the p-T relations obtained from magnetic temperature measurements and from measurements with platinum resistance thermometers, that the uncertainty of p-T relation (6) at 24 °K is at most 10 m°K. If this uncertainty is ascribed only to the inaccuracy in the virial coefficients, used for the calculation of p-T relation (6), the uncertainty in these virial coefficients is restricted to less than 2 %, and the uncertainty in the p-T relation at 14 °K, due to the inaccuracy of the virial coefficients, to about 2 m°K. Together with the uncertainty due to the inaccuracy in L_a , the uncertainty in p-T relation (6) is estimated to be 6 m°K at 14 °K if the temperature of the boiling is chosen to be 20.267 °K.

The uncertainty in dp/dT is estimated to be between 0.1 % and 0.2 % from 14 °K to the boiling point, and between 0.2 % and 0.4 % from the boiling point to 24 °K. It is due to the uncertainty in the virial coefficients that the thermodynamic calculation of the p-T relation above 21 °K from L_a and the virial coefficients does not give a more accurate result than the measurements with platinum resistance thermometers and with magnetic thermometers. Below 21 °K the thermodynamic calculation of the p-T relation gives an accuracy which is quite compatible with the accuracy obtained by other methods.

b. Calculation of the true heat of vaporization

The equation for $L_a(T)$ which has been used for the third (final) approximation of the p-T relation, with the virial coefficients of Woolley e. a. and 20.267 °K for the temperature of the boiling point (eq. 6), is

$$L_a(T) = 1811.469/T + 400.8419 + 37.40083 T - 0.579175 T^2 + 0.0112204 T^3, \quad (7)$$

where $L_a(T)$ is expressed in J/mole. This equation is computed with temperatures derived from the measured pressures using the second approximation of the p-T relation, but as the maximum differences between this second approximation and p-T relation (6) are only a few tenths of a millidegree, eq. (7) may also be used for temperatures expressed in p-T relation (6). The differences between the L_a -values according to eq. (7) and those according to eq. (5) are smaller than 0.005 % between 14 °K and 22 °K, and the difference is about 0.01 % at 24 °K.

Using the equation $L = L_a(1 - V_L/V_G)$ the values of L were calculated at every 0.1 °K. The L_a -values were obtained from eq. (7). For V_L the data of Goodwin, Diller, Roder and Weber ¹⁶⁾ were used. V_G was calculated in the same way as described in section 3 a, using eq. (6) for the relation between p and T, and using the virial coefficients of Woolley e. a. ⁴⁾. Within the accuracy of the

calculations these V_G -values can be represented by

$$^{10}\log V_G = 106.624/T^2 + 10.9680/T + 4.64766 - 0.186845T + 0.0050016T^2 - 0.00006466T^3,$$

where V_G is expressed in cm^3/mole . Table V gives the values of V_G according to this equation for every $^{\circ}\text{K}$. Table V gives also the V_L -values used for the calculation of L .

TABLE V

The molar volume of the saturated vapour of e- H_2 , V_G , calculated from $pV_G = RT(1+B/V_G + C/V_G^2)$, using p-T relation (6) and the virial coefficients of Woolley e. a. ; and the values of V_L used for the calculation of $L(T)$.					
T $^{\circ}\text{K}$	V_G cm^3/mole	V_L cm^3/mole	T $^{\circ}\text{K}$	V_G cm^3/mole	V_L cm^3/mole
14	14526	26.234	20	1618.4	28.360
15	9061.6	26.526	20.267	1506.1	28.481
16	5966.3	26.839	21	1244.2	28.827
17	4104.0	27.176	22	973.20	29.341
18	2926.2	27.539	23	772.32	29.911
19	2149.4	27.932	24	620.26	30.547

To the L -values calculated at every 0.1°K , the following polynomial was fitted by a least squares procedure:

$$L(T) = 747.571/T + 679.6194 + 8.66126T + 0.843677T^2 - 0.0407208T^3, \quad (8)$$

where $L(T)$ is expressed in J/mole .

$L(T)$ can also be calculated from the thermodynamic equation

$$L(T) = L(T_1) + R(T-T_1) - \int_{T_1}^T C_L dT + \int_{T_1}^T C_{Vi} dT + \int_{T_1}^T V_L (dp/dT) dT + R(T\eta - T_1\eta_1) \quad (9)$$

$L(T_1)$ is the value of L at a temperature T_1 , e.g. 20°K . C_L represents the molar heat capacity of the liquid along the saturation line and C_{Vi} the molar heat capacity of the ideal gas at constant volume.

$$\eta = (B - TdB/dT)/V_G + (C - \frac{1}{2} TdC/dT)/V_G^2.$$

η_1 is the value of η at the temperature T_1 . A derivation of eq. (9) has been given by Van Dijk ¹⁷⁾.

The molar heat capacity C_{V_i} for equilibrium hydrogen in the ideal gas state is between 13.8 °K and 24 °K, with sufficient accuracy, independent of the temperature and equal to (3/2) R. Therefore

$$\int_{T_1}^T C_{V_i} dT = \frac{3}{2} R (T - T_1).$$

This value is correct for monoatomic gases, but it can also be used for hydrogen at low temperatures, because practically all molecules are in their lowest rotational and vibrational state (see ref. 4).

$$\int_{T_1}^T V_L (dp/dT)dT \text{ has been replaced by } \frac{1}{2} \left\{ V_L(T) + V_L(T_1) \right\} \Delta p.$$

The value of L (20 °K) calculated from eq. (8) is 901.93 J/mole. For the molar heat capacity C_L of liquid equilibrium hydrogen along the saturation line the representation given by Mullins, Ziegler and Kirk ¹⁸⁾ was used:

$$C_L = 58.84122 - 9.461156 T + 0.6882185 T^2 - 0.02055279 T^3 + 0.000240996 T^4,$$

where C_L is expressed in J/mole °K.

For the calculation of η the B- and C-values of Woolley e. a. (see table II) and p-T relation (6) were used. In table VI the values according to eq. (8) are compared with those calculated from eq. (9).

The increasing difference between the values according to eq. (8) and those obtained from eq. (9) above 22 °K (see table VI) may be due to the uncertainty in the virial coefficients, especially in dB/dT , C and dC/dT , their influence on L being rather large at temperatures above 22 °K. Goodwin ¹⁹⁾ reports values for B and C for equilibrium hydrogen at 24 °K of $-113.2 \text{ cm}^3/\text{mole}$ and $1550 \text{ cm}^6/\text{mole}^2$ respectively. Unfortunately, his measurements did not extend to temperatures below 24 °K, but his reported data for B and C above 24 °K indicate a somewhat higher value for dB/dT and a zero value for dC/dT at 24 °K. Taking $dB/dT = 6.90 \text{ cm}^3/\text{mole } ^\circ\text{K}$ instead of $6.82 \text{ cm}^3/\text{mole } ^\circ\text{K}$, $dC/dT = 0$ and for B and C the

TABLE VI

Calculation of L(T) from eq. (9), using L(20°K) = 901.93 J/mole.							
T °K	$\frac{5}{2} R(T-T_1)$ J/mole	$\int_{T_1}^T C_L dT$ J/mole	$\int_{T_1}^T V_L \frac{dp}{dT} dT$ J/mole	RT η J/mole	L(eq. (9)) J/mole	L(eq. (8)) J/mole	$\frac{\Delta L/L}{100}$
14	-124.715	-97.361	-2.343	- 4.694	908.47	907.90	-0.063
15	-103.929	-83.005	-2.202	- 7.307	912.15	911.77	-0.042
16	- 83.143	-68.086	-1.990	-10.802	914.31	914.11	-0.022
17	- 62.357	-52.444	-1.686	-15.312	914.64	914.60	-0.004
18	- 41.572	-35.949	-1.269	-20.957	912.87	912.92	+0.005
19	- 20.786	-18.496	-0.715	-27.886	908.72	908.79	+0.008
20	0	0	0	-36.248	901.93	901.93	0
21	20.786	19.612	0.904	-46.156	892.29	892.05	-0.027
22	41.572	40.403	2.024	-57.776	879.55	878.89	-0.075
23	62.357	62.437	3.396	-71.307	863.40	862.19	-0.140
24	83.143	85.781	5.053	-86.955	843.53	841.67	-0.221

values given by Goodwin, and keeping $\eta_1 T_1$ unchanged, the L-value at 24 °K, calculated from eq. (9), is equal to 841.3 J/mole. The L-value calculated from the experimental L_a -value changes slightly due to the change of V_G , and becomes 841.5 J/mole. Thus a slight change of the virial coefficients within the accuracy of the available data may give agreement between the L(T) values according to eq. (8) and those according to eq. (9).

If the B-values of Knaap e. a. in combination with the C-values of Woolley e. a., and the p-T relation derived with these virial coefficients (curve 3 in fig. 8) are used for the calculation of V_G and η , the difference $100 \Delta L/L$ between the L(T)-values, calculated from $L_a(T)$, and those, calculated from eq. (9) is equal to - 0.070 at 14 °K and to -0.033 at 24 °K. The differences are slightly larger when the B-values of Knaap e. a. only are used for the calculations of L(T) from $L_a(T)$ and eq. (9): - 0.177 at 14 °K and + 0.260 at 24 °K. Therefore, if the correction term with C and dC/dT is not neglected for the calculation of η , the agreement between the L(T)-values, derived from the experimental $L_a(T)$ -values and the L(T) values, obtained from thermodynamic calculations using the experimental L-value at 20 °K, is satisfactory.

The value of L at 20.267 °K according to eq. (8) is equal to 899.6 J/mole. The agreement with the result of the measurements of Johnston e. a. ⁵⁾, who report a value of 898.7 ± 1.7 J/mole for the heat of vaporization of equilibrium hydrogen at its boiling point, is very satisfactory.

c. The temperature of the triple point

The result of the measurements of the vapour pressure of 20.4 °K-equilibrium hydrogen at its triple point is 52.731 ± 0.010 mm Hg at 0 °C and standard gravity (see section 3). This pressure corresponds

to a temperature of 13.7986 °K in the p-T relation calculated from L_a with the virial coefficients of Woolley e. a. and 20.260 °K for the temperature of the boiling point (curve 4 in fig. 8). The measured pressure corresponds to 13.7978 °K on the T_{L60} scale, which has also 20.260 °K for the temperature of the boiling point.

In p-T relation (6), calculated from L_a with the virial coefficients of Woolley e. a. and 20.267 °K for the temperature of the boiling point, the measured pressure corresponds to a temperature of 13.8018 °K. According to the estimation of the accuracy of p-T relation (6) (see section 3a) the uncertainty in the triple point temperature will be about 6 m°K. Therefore, the result of the triple point measurements is $T_{tr} = 13.802 \pm 0.006$ °K at a pressure of 52.731 ± 0.010 mm Hg at 0 °C and standard gravity, when 20.267 °K is taken for the temperature of the boiling point.

Woolley e. a. ⁴⁾ measured a value of $T_{tr} = 13.813$ °K on the NBS-1939 scale, which corresponds to 13.803 °K on the NBS-1955 scale, at a pressure of 52.8 mm Hg at 0 °C. More recent results are available from the measurements of Barber e. a. ¹³⁾, who found a value of 13.816 °K on the NPL scale at a pressure of 52.95 mm Hg. Therefore, the difference between the NPL scale and p-T relation (6) is 14 m°K at the triple point of equilibrium hydrogen. However the difference between the p-T relation, calculated by Barber e. a. from their measurements of the vapour pressure of equilibrium hydrogen against a platinum resistance thermometer, calibrated on the NPL scale, and p-T relation (6) is only 7 m°K for equal triple point pressures.

In conclusion it can be said, that, if 20.260 °K is taken for the temperature of the boiling point and 52.73 mm Hg for the triple point pressure, the triple point temperature in the p-T relation, derived from L_a with the virial coefficients of Woolley e. a., is in agreement with the triple point temperature on the T_{L60} scale. The triple point temperature in p-T relation (6) is in agreement with the triple point temperature on the NBS - 1955 scale according to Woolley e. a. The triple point temperature in the p-T relation obtained from the provisional results of Van Rijn e. a. ¹⁵⁾, when 20.267 °K is taken for the temperature of the boiling point is 13.798 °K which is also in very good agreement with the value of the triple point temperature obtained from p-T relation (6). It is very satisfactory that the results of the two entirely different methods, the magnetic temperature measurements and the method described in this chapter, are in such a good agreement.

5. Concluding remarks

The p-T relation for equilibrium hydrogen can also be calculated from the thermodynamic equation

$$\ln \frac{p}{p_1} = \left(\frac{L(T_1)}{RT_1} - 1 - \eta_1 \right) \left(1 - \frac{T_1}{T} \right) + \ln \frac{T}{T_1} - \int_{T_1}^T \frac{C_L - C_{Vi}}{RT} dT +$$

$$+ \frac{1}{RT} \int_{T_1}^T (C_L - C_{Vi}) dT + \frac{1}{RT} \int_{T_1}^T V_L \frac{dp}{dt} dT + \epsilon - \epsilon_1,$$

with the boiling point as the reference point. In this equation is

$$\epsilon = \ln \left(1 + B/V_G + C/V_G^2 \right) - (2B/V_G + 3C/2V_G^2).$$

ϵ_1 is the value of ϵ at the temperature T_1 . The other quantities in eq. (10) are the same as those in eq. (9).

Van Dijk¹⁷ derived eq. (10) from the equality of the pressure (p), the temperature (T) and the Gibbs free energies for the two phases of a one component system in equilibrium conditions, by deriving two expressions for the heat of vaporization L as a function of T . When the gaseous equilibrium phase is indicated by an index G and the liquid equilibrium phase by and index L , then

$$U_G + p V_G - T S_G = U_L + p V_L - T S_L \text{ or } H_G - H_L = T(S_G - S_L), \quad (11)$$

where $H = U + pV$.

For both members of eq. (11) an expression for $L(T)$ was derived, L was eliminated from the two expressions and eq. (10) was obtained.

According to the Clausius - Clapeyron equation $(S_G - S_L)$ is equal to $(dp/dT)(V_G - V_L)$, so that eq. (11) can be written as

$$\frac{dp}{dT} = \frac{H_G - H_L}{T(V_G - V_L)}. \quad (12)$$

The derivation of the expression for $L(T)$ from $(H_G - H_L)$ yielded eq. (9). Therefore, eq. (10) can also be obtained by substituting eq. (9) for $(H_G - H_L)$ in eq. (12), and then integrating eq. (12). This integration will be given in an appendix to this chapter.

Eq. (12) can be written in the formulation of eq. (2), which has been used for the calculation described in this thesis. When for the calculation of the p - T relation from eq. (2) L -values, obtained from eq. (9) are used, the result must agree with the p - T relation obtained from the evaluation of eq. (10), assuming that throughout the calculations the same values for the virial coefficients, the specific heat C_L , and the molar volume V_L are used.

As $C_{V_i} = \frac{3}{2} R$ (see reference 4), one finds:

$$\int_{T_1}^T \frac{C_{V_i}}{RT} dT - \frac{1}{RT} \int_{T_1}^T C_{V_i} dT = \frac{3}{2} \ln \frac{T}{T_1} - \frac{3}{2} \left(1 - \frac{T_1}{T} \right),$$

so that eq. (10) can be written as

$$\ln p = \ln p_1 + a \left(1 - \frac{T_1}{T} \right) + \frac{5}{2} \ln T + b + c + \epsilon - \epsilon_1, \quad (10a)$$

in which

$$a = \left(\frac{L(T_1)}{RT_1} - \eta_1 - \frac{5}{2} \right)$$

$$b = \frac{1}{RT} \int_{T_1}^T C_L dT - \int_{T_1}^T \frac{C_L}{RT} dT$$

$$c = \frac{1}{RT} \int_{T_1}^T V_L \frac{dp}{dt} dT .$$

Instead of using T_1 , $L(T_1)$ and η_1 for the calculation of a , one can also calculate this coefficient by taking two reference points, e. g. the boiling point and the triple point of e-H₂.

For both cases $\ln p$ has been evaluated from eq. (10a).

The values of the reference points and of $L(T_1)$, η_1 and ϵ_1 are:

$$T_1 = 20.267 \text{ }^\circ\text{K at } p = 760 \text{ mm Hg at } 0 \text{ }^\circ\text{C}$$

$$T_2 = 13.802 \text{ }^\circ\text{K at } p = 52.73 \text{ mm Hg at } 0 \text{ }^\circ\text{C}$$

$$L(T_1) = 899.60 \text{ J/mole, according to eq. (8)}$$

$\eta_1 = -0.22844$, $\epsilon_1 = 0.09044$, according to the virial coefficients of Woolley e. a.

For the other quantities in eq. (10) the same data have been used as for the calculation of L from eq. (9).

When only T_1 is used as a reference point, the value of a, denoted by a_1 , is equal to 3.06711. When T_1 and T_2 are used as reference points the value of a, denoted by a_2 , is equal to 3.06843.

In table VIIA the values of the individual terms of eq. (10a) are given.

Table VIIB gives the values of $\ln p_{th1}$, calculated from eq. (10a) with only T_1 as a reference point, and the values of $\ln p_{th2}$, calculated with T_1 and T_2 as reference points.

ΔT_{thx} , in which x may be 1 or 2, is the difference $T_{thx} - T_{La}$, in which T_{thx} is the temperature corresponding to $\ln p_{thx}$ and T_{La} is the temperature derived from eq. (6).

TABLE VII A

Calculation of $\ln p$ from $\ln p = \ln p_1 + a(1 - \frac{T_1}{T}) + \frac{5}{2} \ln \frac{T}{T_1} + b + c + \epsilon - \epsilon_1$						
T $^{\circ}K$	$a_1(1 - \frac{T_1}{T})$	$a_2(1 - \frac{T_1}{T})$	$\frac{5}{2} \ln \frac{T}{T_1}$	b	c	ϵ
14	-1.37297	-1.37356	-0.92484	-0.16002	-0.02196	0.01660
16	-0.81796	-0.81831	-0.59101	-0.06478	-0.01659	0.03315
18	-0.38629	-0.38645	-0.29656	-0.01629	-0.00995	0.05641
20	-0.04095	-0.04096	-0.03315	-0.00020	-0.00133	0.08606
22	+0.24160	+0.24171	+0.20512	-0.00788	+0.00986	0.12149
23	+0.36445	+0.36461	+0.31625	-0.01882	+0.01660	0.14114
24	+0.47706	+0.47727	+0.42265	-0.03379	+0.02420	0.16196

a_1 : value of a using 1 reference point
 a_2 : value of a using 2 reference points.

TABLE VII B

$\ln p$, obtained from table VII A. $T_{thx} = T_{thx} - T_{La}$				
T $^{\circ}K$	$\ln p_{th1}$	ΔT_{th1} $m^{\circ}K$	$\ln p_{th2}$	ΔT_{th2} $m^{\circ}K$
14	4.07969	-0.8	4.07910	+0.2
16	5.08569	-1.1	5.08534	-0.2
18	5.89020	-0.6	5.89004	-0.2
20	6.55331	-0.1	6.55330	-0.1
22	7.11307	-0.3	7.11318	-0.7
23	7.36250	-0.9	7.36266	-1.5
24	7.59496	-2.0	7.59517	-2.9

The differences ΔT_{th1} and ΔT_{th2} are also shown in fig. 10. As had to be expected from the agreement between the calculated L-values according to table VI, and the experimental values according to eq. (8), the agreement between the temperatures derived from eq. (10) and those according to eq. (6) is good.

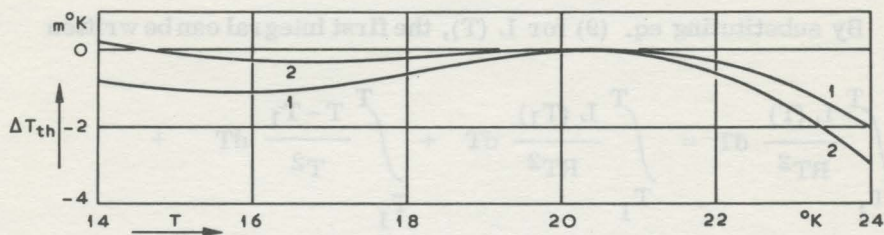


FIG. 10. Temperature differences $T_{th} - T$. T according to eq. (6). T_{th} according to eq. (10) to eq. (10).

1. T_{th} calculated with only 20.267 °K as a reference point.
2. T_{th} calculated with 20.267 °K and 13.802 °K as reference points.

APPENDIX

Integration of eq. (12).

By substitution of $V_G = RT(1+Z_G)/p$, in which Z_G is the correction for the non ideality of the gas, and of $H_G - H_L = L(T)$, eq. (12) can be written as

$$\frac{dp}{dT} = \frac{L(T)}{\frac{RT^2}{p} (1 + Z_G - pV_L/RT)}$$

$$\begin{aligned} \text{or } \frac{d \ln p}{dT} &= \frac{L(T)}{RT^2 (1 + Z_G - pV_L/RT)} \\ &= \frac{L(T)}{RT^2} - \frac{Z_G}{p} \frac{dp}{dT} + \frac{V_L}{RT} \frac{dp}{dT} \end{aligned}$$

Integration of this expression from T_1 to T yields

$$\ln \frac{p}{p_1} = \int_{T_1}^T \frac{L(T)}{RT^2} dT - \int_{T_1}^T \frac{Z_G}{p} \frac{dp}{dT} dT + \frac{1}{R} \int_{T_1}^T \frac{V_L}{T} \frac{dp}{dT} dT. \quad (A)$$

By substituting eq. (9) for $L(T)$, the first integral can be written as

$$\begin{aligned} \int_{T_1}^T \frac{L(T)}{RT^2} dT &= \int_{T_1}^T \frac{L(T_1)}{RT^2} dT + \int_{T_1}^T \frac{T - T_1}{T^2} dT + \\ &+ \int_{T_1}^T \frac{\int_{T_1}^T (C_{Vi} - C_L) dT}{RT^2} dT - \int_{T_1}^T \frac{\int_{T_1}^T V_L \frac{dp}{dT} dT}{RT^2} dT + \\ &+ \int_{T_1}^T \frac{(T\eta - T_1 \eta_1)}{T^2} dT = \\ &= -\frac{L(T_1)}{RT} + \frac{L(T_1)}{RT_1} + \ln \frac{T}{T_1} + \frac{T_1}{T} - 1 + \\ &-\frac{1}{R} \int_{T_1}^T \left[\int_{T_1}^T (C_{Vi} - C_L) dT \right] d\frac{1}{T} dT + \\ &+ \frac{1}{R} \int_{T_1}^T \left[\int_{T_1}^T V_L \frac{dp}{dT} dT \right] d\frac{1}{T} dT + \int_{T_1}^T \frac{\eta}{T} dT + \frac{T_1 \eta_1}{T} - \eta_1 = \end{aligned}$$

$$\begin{aligned}
 &= \left(\frac{L(T_1)}{RT_1} - 1 - \eta_1 \right) \left(1 - \frac{T_1}{T} \right) + \ln \frac{T}{T_1} + \int_{T_1}^T \frac{C_{V_i} - C_L}{RT} dT + \\
 &- \frac{1}{RT} \int_{T_1}^T (C_{V_i} - C_L) dT + \frac{1}{RT} \int_{T_1}^T V_L \frac{dp}{dT} dT - \frac{1}{R} \int_{T_1}^T \frac{V_L}{T} \frac{dp}{dT} dT + \int_{T_1}^T \frac{\eta}{T} dT.
 \end{aligned}$$

The last but one integral in this expression is the same as the last one of expression (A), with opposite sign. Therefore, expression (A) becomes

$$\begin{aligned}
 \ln \frac{p}{p_1} &= \left(\frac{L(T_1)}{RT_1} - 1 - \eta_1 \right) \left(1 - \frac{T_1}{T} \right) + \ln \frac{T}{T_1} + \\
 &+ \int_{T_1}^T \frac{C_{V_i} - C_L}{RT} dT - \frac{1}{RT} \int_{T_1}^T (C_{V_i} - C_L) dT + \\
 &+ \frac{1}{RT} \int_{T_1}^T V_L \frac{dp}{dT} dT + \int_{T_1}^T \frac{\eta}{T} dT - \int_{T_1}^T \frac{Z_G}{p} \frac{dp}{dT} dT. \quad (B)
 \end{aligned}$$

From the equation of state $p = RT(1+Z_G)/V_G$ follows

$$\begin{aligned}
 \frac{dp}{dT} &= R(1+Z_G)/V_G + \frac{RT}{V_G} \frac{dZ_G}{dT} - \frac{RT(1+Z_G)}{V_G^2} \frac{dV_G}{dT} = \\
 &= \frac{p}{T} + \frac{p}{1+Z_G} \frac{dZ_G}{dT} - \frac{p}{V_G} \frac{dV_G}{dT}
 \end{aligned}$$

By definition:

$$\eta = Z_G + \int_{T, V_i}^{T, V_G} \frac{T}{V} \left(\frac{\delta Z}{\delta T} \right)_V dV \quad (\text{see ref. 17})$$

$$\text{so that } \frac{\eta}{T} - \frac{Z_G}{p} \frac{dp}{dT} = \int_{T, V_i}^{T, V_G} \frac{1}{V} \left(\frac{\delta Z}{\delta T} \right)_V dV - \frac{Z_G}{1+Z_G} \frac{dZ_G}{dT} + \frac{Z_G}{V_G} \frac{dV_G}{dT}$$

The quantity ϵ in eq. (10) is by definition equal to

$$\epsilon = \ln(1 + Z_G) - Z_G + \int_{T, V_i}^{T, V_G} \frac{Z}{V} dV$$

$$\frac{d\epsilon}{dT} = \frac{1}{1+Z_G} \frac{dZ_G}{dT} - \frac{dZ_G}{dT} + \int_{T, V_i}^{T, V_G} \frac{1}{V} \left(\frac{\delta Z}{\delta T} \right)_V dV + \frac{Z_G}{V_G} \frac{dV_G}{dT}$$

$$\text{so that } \frac{\eta}{T} - \frac{Z_G}{p} \frac{dp}{dT} = \frac{d\epsilon}{dT}$$

Substituting this expression in the last two terms of expression (B), the result of the integration of eq. (12) is:

$$\ln \frac{p}{p_1} = \left(\frac{L(T_1)}{RT_1} - 1 - \eta_1 \right) \left(1 - \frac{T_1}{T} \right) + \ln \frac{T}{T_1} + \int_{T_1}^T \frac{C_{V_i} - C_L}{RT} dT + \frac{1}{RT} \int_{T_1}^T (C_{V_i} - C_L) dT + \frac{1}{RT} \int_{T_1}^T V_L \frac{dp}{dT} dT + \epsilon - \epsilon_1$$

CHAPTER IV

THE HEAT OF VAPORIZATION OF HELIUM-FOUR

1. Introduction

Experimental data concerning the heat of vaporization of helium as a function of temperature are available from the measurements of Dana and Kamerlingh Onnes ²⁰⁾ and from those of Berman and Mate ²¹⁾.

Dana and Kamerlingh Onnes measured the true heat of vaporization of helium at and below the boiling point, determining directly the amount of liquid which had been evaporated. As remarked in chapter I, the accuracy of this method will not be better than 0.5 to 1 %.

Berman and Mate measured the apparent heat of vaporization of helium between 2.2 °K and 5.15 °K. They estimated the accuracy of their results to be a few tenths of 1 %.

When Clapeyron's equation is used in the formulation $dp/dT = L_a/TV_G$, in which dp/dT and T are taken according to the 1958 - ⁴He scale ²²⁾, V_G can be calculated from L_a . When it is assumed that dp/dT is accurate within 0.2 % and that T is accurate within 0.1 %, the V_G -values, calculated in this way from the L_a -values of Berman and Mate, should be accurate within about 0.5 %. However, the differences between these V_G -values and those obtained by Edwards and Woodbury ²³⁾ from their measurements of the refractive index of the saturated vapour of helium are 2.7 % at 4.2 °K and 3.5 % at 5 °K. Edwards and Woodbury estimate the accuracy of the results of their measurements to be better than 0.5 % between 4.2 °K and 5 °K, so that in this temperature range the V_G -values according to Edwards and Woodbury differ from those calculated from the L_a -values according to Berman and Mate by about three times the combined estimated errors.

Therefore, the measurements described in this chapter were performed in order to obtain more information concerning the heat of vaporization and the molar volume of the saturated vapour of helium-four.

2. The experiments

For the measurements of the heat of vaporization of helium the same apparatus has been used and the same procedure has been followed as for the measurements on hydrogen (see chapter II).

The apparent heat of vaporization of helium has been measured between 2.2 °K and 5 °K. Below the λ -point, 2.172 °K, it was not possible to obtain reliable results with this apparatus, because of the large heat leak caused by the helium film in the capillaries between the calorimeter reservoir A and the copper block B (see fig. 1) Furthermore, the low pressure in the calorimeter reservoir below

2.2 °K restricts the accuracy of the measurement of the amount of evaporated gas, because the pressure in the vessel I or II had to be at least 10 mm Hg lower than the pressure in the calorimeter reservoir to obtain an adjustable gas flow from the calorimeter reservoir into the vessels I and II.

As remarked in chapter II, the length of the foreperiod has to be sufficiently long to establish temperature equilibrium in the capillaries between the calorimeter and the cap of the cryostat. Above 4.5 °K, however, the length of the foreperiod which is required to obtain temperature equilibrium in the capillaries is so long that at the end of the foreperiod not enough liquid helium is left in the reservoir for the measuring-period. Therefore, at 4.5 °K and at higher temperatures, different lengths of the foreperiods were used and the results for L_a were extrapolated to infinite length of the foreperiod.

The accuracy of the results obtained in this way is estimated to be not better than 0.3 %. As the results were found to be, within this accuracy, in agreement with the results of Berman and Mate, the measurements were not extended to temperatures above 5 °K.

3. Experimental results for L_a

The results of the measurements of the apparent heat of vaporization of helium-four between 2.2 °K and 5 °K are listed in table VIII. In this table also the pressure in the calorimeter during the evaporation, the temperature derived from this pressure using the 1958-⁴He scale, the length of the measuring-period, the amount of heat supplied to the calorimeter and the amount of gas liberated from the calorimeter are given.

The heater resistance is given by

$$R = \left\{ 107.70 + 0.037 (T - 4.25) \right\} \Omega, \text{ in the temperature range from}$$

2.2 °K to 5 °K.

The amount of gas liberated from the calorimeter has been calculated from the pressure p , the temperature T and the volume V of the gas in the vessels I and II, using the equation $n(1+nB/V) = pV/RT$. For the value of B for ⁴He at room temperature 11 cm³/mole has been taken, according to the adopted values of Keesom²⁴).

In fig. 11 the experimental L_a -values of table VIII are shown as a function of the temperature.

Smoothed values of L_a at every 0.1 °K between 2.2 °K and 5 °K were obtained from a figure, similar to fig. 11, drawn on a large scale. Below 3 °K it was difficult to decide how to draw the curve through the experimental points, due to the inflection point in the L_a -curve at about 2.6 °K. Therefore, below 3 °K small corrections were applied to the L_a -values read from the graph, in such a way, that the V_G -values, calculated from the L_a -values at every 0.1 °K,

TABLE VIII

Experimental results of L_a of ${}^4\text{He}$					
P mm Hg 0°C	T_{58} $^\circ\text{K}$	time s	$i^2 R t$ joule	$10^3 n_a$ mole	L_a joule mole
43.57	2.232	2103.6	1.4143	15.359	92.08
43.57	2.232	2107.2	1.4164	15.390	92.03
43.74	2.233	2638.0	2.5559	27.794	91.96
57.91	2.358	3003.3	2.0206	21.729	92.99
57.91	2.358	3009.5	2.0243	21.825	92.75
58.02	2.359	1803.5	1.7472	18.788	92.99
58.02	2.359	1801.9	1.7451	18.798	92.83
77.63	2.501	2709.8	2.6369	28.102	93.83
77.63	2.501	2703.2	2.6302	28.023	93.86
77.95	2.503	1509.0	2.6056	27.766	93.84
77.95	2.503	1512.3	2.6111	27.819	93.86
122.33	2.750	2403.8	4.1401	43.121	96.01
122.33	2.750	2407.4	4.1449	43.297	95.73
122.43	2.751	4509.4	4.3713	45.530	96.01
122.43	2.751	4510.7	4.3705	45.553	95.94
176.06	2.978	3639.3	6.2883	64.623	97.31
177.32	2.982	2413.2	6.5078	66.819	97.39
177.32	2.982	2421.9	6.5290	67.152	97.23
177.38	2.983	3606.1	6.2310	64.029	97.32
177.38	2.983	3602.5	6.2232	64.025	97.20
180.73	2.995	2440.2	6.5761	67.625	97.24
257.46	3.245	1981.8	5.3426	54.291	98.41
257.46	3.245	1862.5	5.0190	50.994	98.42
258.46	3.248	2402.6	6.4686	65.608	98.59
258.46	3.248	2411.0	6.4884	65.991	98.32
258.64	3.248	3603.1	6.2115	63.019	98.57
258.64	3.248	3603.8	6.2094	63.106	98.40
344.59	3.473	2049.5	5.5314	55.882	98.98
344.59	3.473	2102.4	5.6716	57.360	98.88
356.06	3.501	2103.4	5.6738	57.334	98.96
356.06	3.501	2103.0	5.6714	57.440	98.74
356.37	3.501	3304.2	5.7081	57.694	98.94
356.37	3.501	3303.5	5.7055	57.791	98.73
467.40	3.737	2085.5	5.6236	56.949	98.75
467.53	3.737	1922.4	5.1842	52.497	98.75
467.53	3.737	1983.0	5.3460	54.135	98.75
612.55	3.994	2002.2	5.3969	55.190	97.79
613.39	3.995	2192.3	5.9096	60.473	97.72
783.79	4.248	2400.6	6.4736	67.622	95.73
783.79	4.248	2401.6	6.4740	67.595	95.78
784.39	4.249	3325.3	5.7424	59.945	95.79
786.70	4.252	3304.5	5.7077	59.565	95.82
786.70	4.252	3606.9	6.2283	65.068	95.72
983.7	4.501	1953.6	5.2662	56.857	92.62
983.7	4.501	1923.2	5.1810	55.966	92.57
1211.9	4.749	1984.6	5.3537	60.784	88.08
1211.9	4.749	2011.2	3.4752	39.589	87.78
1212.0	4.749	2266.8	3.9186	44.483	88.09
1212.1	4.749	2055.3	3.5473	40.366	87.88
1484.2	5.005	1812.5	2.7532	35.410	77.75
1484.2	5.005	1204.3	1.8301	23.491	77.91

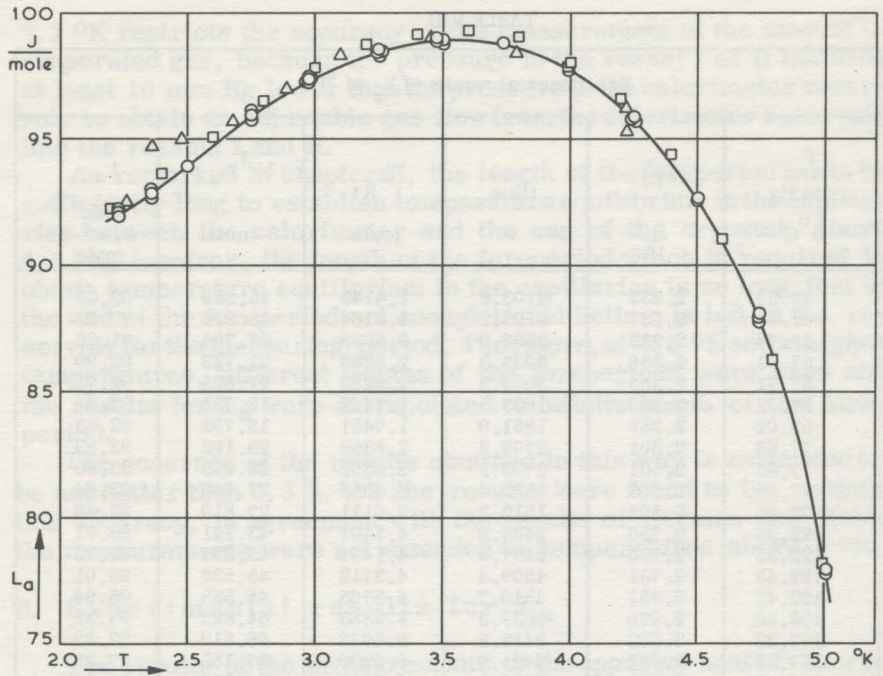


FIG. 11. Experimental values of L_a of helium versus T .

- This research according to table VIII.
- △ Recalculated values of Dana and Kamerlingh Onnes.
- Smoothed values of Berman and Mate.
- Smoothed values of this research.

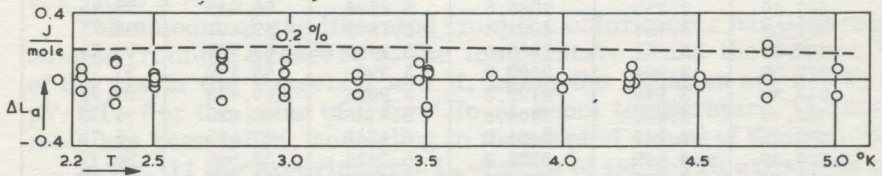


FIG. 12. Deviations of the experimental L_a -values according to table VIII from the smoothed values.

$$\Delta L_a = L_a(\text{table VIII}) - L_a(\text{smoothed}).$$

which were decreasing regularly from 3 °K to 5 °K, were also decreasing regularly from 2.2 °K to 3 °K.

TABLE IX

Smoothed values of L_a and L of ^4He				
T °K	L_a	V_L	dp/dT	L
	$\frac{\text{joule}}{\text{mole}}$	$\frac{\text{cm}^3}{\text{mole}}$	$\frac{\text{mm Hg}}{\text{°K}}$	$\frac{\text{joule}}{\text{mole}}$
2.2	91.85	27.44	97.31	91.07
2.3	92.47	27.51	113.9	91.51
2.4	93.11	27.60	132.1	91.94
2.5	93.85	27.71	151.9	92.45
2.6	94.65	27.83	173.2	92.98
2.7	95.47	27.96	195.9	93.50
2.8	96.20	28.11	219.9	93.89
2.9	96.84	28.26	245.4	94.16
3.0	97.39	28.43	272.3	94.29
3.1	97.86	28.62	300.7	94.30
3.2	98.25	28.82	330.6	94.19
3.3	98.57	29.04	361.9	93.95
3.4	98.79	29.27	394.6	93.56
3.5	98.90	29.52	428.7	92.99
3.6	98.91	29.79	464.1	92.27
3.7	98.80	30.09	500.9	91.37
3.8	98.57	30.41	539.1	90.26
3.9	98.22	30.77	578.9	88.96
4.0	97.73	31.10	620.6	87.44
4.1	97.08	31.59	663.7	85.62
4.2	96.27	32.07	708.1	83.55
4.3	95.27	32.61	754.1	81.17
4.4	94.05	33.21	802.9	78.41
4.5	92.62	33.89	853.5	75.27
4.6	90.96	34.68	906.0	71.69
4.7	89.02	35.63	960.5	67.58
4.8	86.59	36.78	1017	62.65
4.9	83.26	38.23	1076	56.39
5.0	78.17	40.22	1137	47.68

For the calculation of V_G the equation $V_G = L_a / (T dp/dT)$ has been used. dp/dT and T have been taken from the 1958 - ^4He scale.

The smoothed L_a -values are given in table IX and are represented by the full drawn curve in fig. 11. Fig. 12 shows the differences between the experimental L_a -values according to table VIII and the smoothed L_a -values according to table IX.

4. Discussion of the results

Figure 12 shows that the deviation of the mean value of the experimental results at a certain temperature from the smoothed value at that temperature is small. It is smaller than 0.12 % in the whole temperature range from 2.2 °K to 5 °K. The inaccuracy in the smoothed values will be smaller than the maximum deviation.

Therefore, the inaccuracy in the smoothed L_a -values, due to random errors, is estimated to be not more than 0.1 %.

The uncertainty in the L_a -values, due to possible systematic errors in the measured quantities, is estimated to be 0.03 %. This uncertainty is somewhat larger than the uncertainty in the results of the measurements on hydrogen, due to the less reproducible results of the calibrations of the heater resistance in the liquid helium temperature range.

In conclusion, the total inaccuracy in the smoothed L_a -values, given in table IX, is estimated to be ≤ 0.13 % below 4.5 °K and increases above 4.5 °K to 0.35 % at 5 °K. The increase of the uncertainty above 4.5 °K is mainly due to the large amount of gas in the capillaries as mentioned at the end of section 2.

In fig. 11 also the smoothed L_a -values of Berman and Mate ²¹⁾ and the recalculated results of Dana and Kamerlingh Onnes ²⁰⁾ are given. The L_a -values of Berman and Mate have been corrected for the difference between the 1958-⁴He scale and the 55E-⁴He scale. The latter scale has been used by Berman and Mate. Good agreement is found for the temperature dependence of L_a , whereas the differences between the L_a -values are within the combined estimated errors of both sets of measurements.

The results of Dana and Kamerlingh Onnes have been recalculated from the data for the pressure, the volume of the evaporated liquid and the amount of heat supplied to the calorimeter, given in their paper. For the calculation of the amount of moles from the volume of the evaporated liquid, the molar volumes calculated from the data of Edwards ²⁵⁾ for the refractive index of liquid helium under its saturation pressure have been used. Within the accuracy of the measurements the recalculated results of Dana and Kamerlingh Onnes are in agreement with the results of the measurements described in this chapter.

5. Calculation of the true heat of vaporization

The true heat of vaporization, L , has been calculated from the smoothed L_a -values with the equation $L = L_a (1 - V_L/V_G)$, or; as $1/V_G = (T dp/dT)/L_a$, $L = L_a - TV_L dp/dT$. The values for V_L were obtained from the data of Edwards ²⁵⁾. T and dp/dT have been taken according to the 1958-⁴He scale. The L -values, obtained from these calculations, are given in table IX.

6. Calculation of the molar volume, V_G , of the saturated vapour of ⁴He from L_a

V_G -values have been calculated from the L_a -values according to table IX with the equation $V_G = L_a/(T dp/dT)$. $T dp/dT$ has been taken according to the 1958 - ⁴He scale. The V_G -values obtained in this way, and denoted by $V_G(1)$, are listed in table X.

As already mentioned in section 1 of this chapter, the differences between the V_G -values obtained from the L_a -values of Berman

TABLE X

The molar volume, $V_G(x)$, of the saturated vapour of ^4He . Unit of V_G : cm^3/mole . Explanation of x in the text.				
T $^{\circ}\text{K}$	$V_G(1)$	$V_G(2)$	$V_G(3)$	$V_G(4)$
2.2	3218	3193	3208	3203
2.3	2648	2617	2636	2633
2.4	2203	2186	2196	2194
2.5	1853.6	1841.7	1849.8	1848.1
2.6	1576.6	1565.2	1573.5	1572.4
2.7	1353.8	1344.4	1350.0	1349.3
2.8	1171.7	1159.5	1167.2	1166.8
2.9	1020.6	1012.4	1016.0	1015.9
3.0	894.2	887.4	889.9	890.0
3.1	787.4	781.1	783.5	783.9
3.2	696.6	691.4	693.2	693.7
3.3	619.1	615.3	615.9	616.5
3.4	552.3	549.7	549.3	550.0
3.5	494.4	492.6	491.5	492.3
3.6	444.1	442.0	441.1	441.9
3.7	399.9	397.3	396.9	397.7
3.8	360.9	357.3	357.9	358.7
3.9	326.3	321.5	323.2	324.1
4.0	295.3	291.1	292.3	293.2
4.1	267.6	262.2	264.4	265.3
4.2	242.8	237.2	239.3	240.2
4.3	220.4	214.5	216.4	217.3
4.4	199.68	194.9	195.2	196.1
4.5	180.88	176.46	175.3	176.2
4.6	163.71	159.33	156.2	157.1
4.7	147.91	143.51	136.3	137.0
4.8	133.04	128.62	-	-
4.9	118.45	114.33	-	-
5.0	103.13	100.15	-	-

and Mate ²¹⁾ and the V_G -values obtained from the refractive index measurements of Edwards and Woodbury ²³⁾ are 2.7 % at 4.2 $^{\circ}\text{K}$ and 3.5 % at 5 $^{\circ}\text{K}$, the V_G -values of Edwards and Woodbury being the lower ones. Our L_a -values are in general merely 0.4 % lower than those of Berman and Mate. Therefore, the differences between the V_G -values calculated from our L_a -values, and the V_G -values calculated from the results of Edwards and Woodbury, are still larger than can be explained from the combined estimated errors in both sets of measurements.

In the following section the $V_G(1)$ -values will be compared in detail with the V_G -values obtained by Edwards and Woodbury and with the V_G -values calculated from the equation of state.

7. Comparison of $V_G(1)$ with other V_G -values

In table X different values for V_G are given. The values denoted by $V_G(1)$ are calculated from the smoothed L_a -values given in table IX.

The values denoted by $V_G(2)$ are obtained from the results of Edwards and Woodbury ²³⁾ from their measurements of the refractive index of helium.

The values denoted by $V_G(3)$ are calculated from the equation of state $pV_G = RT (1 + B/V_G + C/V_G^2)$, using for B Keesom's equation ²⁴⁾ $B = (0.6824 - 17.244/T)22.427 \text{ cm}^3/\text{mole}$ and for C the equation $C = (5 \times 10^3/T - 4.86 \times 10^6/T^6) \text{ cm}^6/\text{mole}^2$, according to an analysis of Van Dijk and Ter Harmsel ²⁶⁾.

The values denoted by $V_G(4)$ are calculated from the equation of state, using for B the values given by Kilpatrick, Keller and Hammel ²⁷⁾ and for C the equation $C = (1500/\sqrt{T} - 7.5 \times 10^6/T^7) \text{ cm}^6/\text{mole}^2$, according to Clement's analysis ²⁸⁾.

The relative differences between the V_G -values, $\{V_G(x) - V_G(1)\} / V_G(1)$, are shown in fig. 13.

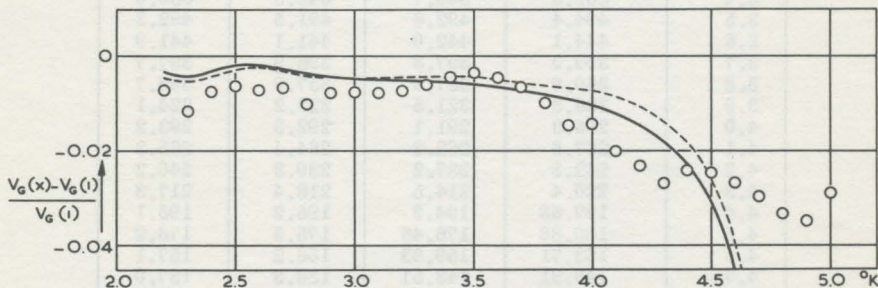


FIG. 13. Comparison of different data for the molar volume, V_G , of the saturated vapour of ^4He . $\Delta V_G(x) = V_G(x) - V_G(1)$.

$V_G(1)$ calculated from L_a and the 1958- ^4He scale.

o $V_G(2)$ according to Edwards and Woodbury ²³⁾

— $V_G(3)$ } calculated from the equation of state $pV_G =$

---- $V_G(4)$ } $RT (1 + B/V_G + C/V_G^2)$, using different data for B and C.

Above 4.7 °K the equation of state does not give a real value for V_G , when the virial coefficients mentioned above and the 1958- ^4He scale are used. This is shown on an example in fig. 14, where p is given as a function of $1/V$ at $T = 4.8 \text{ °K}$ according to the equation of state. For B and C the functions mentioned above for the calculations of $V_G(3)$ have been used. V is the molar volume of the unsaturated vapour at a pressure p . Because the saturation pressure of ^4He at 4.8 °K according to the 1958- ^4He scale (indicated in fig. 14 by a dashed line) is higher than the maximum pressure according to the equation of state, this equation does not give a real value for the molar volume of the saturated vapour.

In section 4 the accuracy of the smoothed L_a -values has been estimated to be 0.13 % below 4.5 °K.

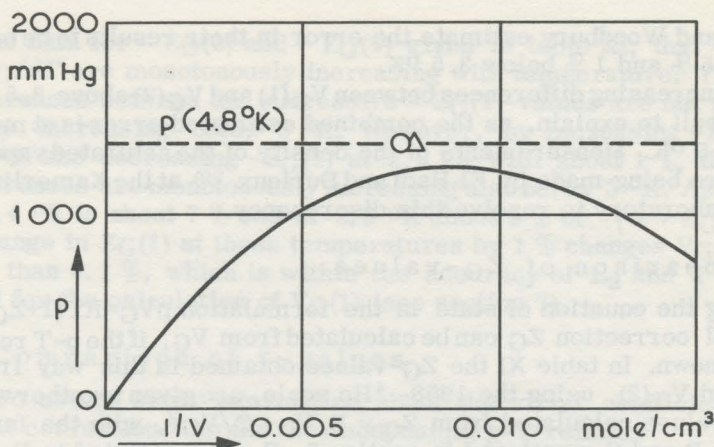


FIG. 14. p versus $1/V$ at 4.8°K according to the equation of state $p = RT(1 + B/V + C/V^2)/V$
 $\circ V_G(1)$, calculated from L_a
 $\Delta V_G(2)$, according to Edwards and Woodbury ²³

If we assume an inaccuracy of 0.2 % in dp/dT and of $2 \text{ m}^{\circ}\text{K}$ in the p - T relation used for the calculation of $V_G(1)$, the maximum error in $V_G(1)$ will be about 0.4 %. It must be remarked that an error in the p - T relation influences $V_G(1)$ and $V_G(3)$ in opposite directions. When T is changed by 0.1 %, the difference $\{V_G(3) - V_G(1)\} / V_G(1)$ changes by 0.002. Therefore, the uncertainty in the p - T relation and in L_a is sufficient to explain the differences between $V_G(3)$ and $V_G(1)$ below 3.5°K .

Furthermore, an inaccuracy of 1 % in the values of $Z_G = B/V_G + C/V_G^2$ gives an inaccuracy in $V_G(3)$ of 0.05 % at 2.2°K and of 0.13 % at 3°K , as can be concluded from table XI. In this table the values of $Z_G(x)$ are given. $Z_G(x) = \{p V_G(x)/RT\} - 1$.

Therefore, below 4.2°K the differences between $V_G(1)$ and $V_G(3)$ are within the accuracy of the measurements of L_a and of the available data for the p - T relation and the virial coefficients.

The increase of the differences between $V_G(1)$ and $V_G(3)$ above 4.2°K is most probably due to the use of only the second and third virial coefficient in the equation of state for the calculation of $V_G(3)$. As already remarked, the equation of state does not give a real value for V_G at temperatures above 4.7°K , when only the functions for B and C , which are given above, are used. Above 4.2°K the use of only these functions may not be sufficient for accurate calculation of the molar volume of the saturated vapour.

The discussion given above for $V_G(3)$ holds also for $V_G(4)$, as the differences between $V_G(3)$ and $V_G(4)$ are small.

Below 3.5°K the differences between $V_G(1)$ and $V_G(2)$ are smaller than or equal to the combined estimated errors in the V_G -values. As already remarked, the estimated error in $V_G(1)$ is about 0.4 %.

Edward and Woodbury estimate the error in their results to be between 0.5 % and 1 % below 3.5 °K.

The increasing differences between $V_G(1)$ and $V_G(2)$ above 3.5 °K are difficult to explain, as the combined estimated error is at most 1.2 % at 5 °K. Measurements of the density of the saturated vapour of ^4He are being made by El Hadi and Durieux²⁹⁾ at the Kamerlingh Onnes Laboratory to resolve this discrepancy.

8. Comparison of Z_G -values.

Using the equation of state in the formulation $pV_G = RT(1 + Z_G)$, the virial correction Z_G can be calculated from V_G , if the p-T relation is known. In table XI the Z_G -values obtained in this way from $V_G(1)$ and $V_G(2)$, using the 1958- ^4He scale, are given together with the Z_G -values calculated from $Z_G = B/V_G + C/V_G^2$, with the functions for B and C mentioned in section 7. $Z_G(3)$ is related to $V_G(3)$ and $Z_G(4)$ to $V_G(4)$.

TABLE XI

Values of $Z_G(x)$ for ^4He . Explanation of x in the text.				
T °K	$-Z_G(1)$	$-Z_G(2)$	$-Z_G(3)$	$-Z_G(4)$
2.2	0.0509	0.0583	0.0540	0.0552
	0.0174	0.0171	0.0173	0.0170
2.4	0.0683	0.0754	0.0713	0.0722
	203	198	191	188
2.6	0.0886	0.0952	0.0904	0.0910
	193	220	209	206
2.8	0.1079	0.1172	0.1113	0.1116
	219	192	227	223
3.0	0.1298	0.1364	0.1340	0.1339
	245	242	245	240
3.2	0.1543	0.1606	0.1585	0.1579
	260	235	262	258
3.4	0.1803	0.1841	0.1847	0.1837
	275	275	285	280
3.6	0.2078	0.2116	0.2132	0.2117
	297	335	306	304
3.8	0.2375	0.2451	0.2438	0.2421
	327	354	338	332
4.0	0.2702	0.2805	0.2776	0.2753
	352	409	378	375
4.2	0.3054	0.3214	0.3154	0.3128
	395	392	442	438
4.4	0.3449	0.3606	0.3596	0.3566
	439	445	572	569
4.6	0.3888	0.4051	0.4168	0.4135
	498	521	-	-
4.8	0.4386	0.4572	-	-
	724	679	-	-
5.0	0.5110	0.5251	-	-

From the calculations of $-Z_G$ as a function of T with the functions for B(T) and C(T) mentioned above, it may be expected according

to the data for $-Z_G(3)$ and $-Z_G(4)$ given in table XI, that $-Z_G$ and $-dZ_G/dT$ are monotonously increasing with temperature. The first differences between the successive $-Z_G(1)$ -values are not monotonously increasing below 3 °K. However, by increasing $-Z_G(1)$ at 2.4 °K and decreasing $-Z_G(1)$ at 2.6 °K with about 1 %, the first differences are monotonously increasing also below 3 °K. As $-Z_G(1)$ at 2.4 °K is about 7 % and at 2.6 °K about 9 % of $\{1 + Z_G(1)\}$, a change in $Z_G(1)$ at these temperatures by 1 % changes $V_G(1)$ with less than 0.1 %, which is within the accuracy of L_a and $T dp/dT$, used for the calculation of $V_G(1)$ (see section 7).

9. Comparison of ϵ -values

To obtain more information about the virial coefficients the virial correction ϵ in the thermodynamic p-T relation

$$\ln p = i'_0 - \frac{L_0}{RT} + \frac{5}{2} \ln T - \frac{1}{RT} \int_0^T S_L dT + \frac{1}{RT} \int_0^T V_L \frac{dp}{dT} dT + \epsilon \quad (13)$$

has been calculated in different ways with p and T according to the 1958-⁴He scale. A derivation of eq. (13) has been given by Van Dijk and Durieux³⁰⁾.

The quantities in eq. (13) are:

$i'_0 = 12.2440$ c. g. s. units.

$R = 8.31432$ joule/mole °K.

L_0 is the heat of vaporization of ⁴He at 0 °K. $L_0 = 59.62$ joule/mole (see ref. 22). S_L is the entropy of liquid ⁴He along the saturation line.

$\int_0^T S_L dT$ has been taken according to the data of Clement³¹⁾.

V_L is the molar volume of liquid ⁴He under its saturation pressure. The values for V_L have been taken according to the data of Edwards²⁵⁾.

$$\epsilon = \ln(1 + Z_G) - Z_G + \int_{T, V_i}^{T, V_G} \frac{Z}{V} dV.$$

V_i is the molar volume of the gas which is large enough to treat it as an ideal gas.

The ϵ -values calculated from eq. (13) are denoted by ϵ_{58} .

When Z_G is approximated by $Z_G = B/V_G + C/V_G^2$, the expression for ϵ yields $\epsilon = \ln(1+Z_G) - 2Z_G + \frac{1}{2} C/V_G^2$. Since it is not possible to calculate $\frac{1}{2} C/V_G^2$ from Z_G , this term has to be estimated for the calculation of $\epsilon(1)$ from $Z_G(1)$.

When ϵ is calculated with the B- and C-values (B(3) and C(3)) as used for the calculation of $V_G(3)$ (see section 7), the value of $\frac{1}{2} C(3)/V_G^2(3)$ is - 4 % of the value of $\epsilon(3)$ at 2.2 °K, it is zero at about 3.95 °K and it increases to about 4 % of $\epsilon(3)$ at 4.6 °K.

Therefore, below 4.2 °K the error in $\epsilon(1)$ will be small when the values of $\frac{1}{2} C(3)/V_G^2(3)$ are used for the calculation of $\epsilon(1)$. Above 4.2 °K the use of these values will give increasing uncertainties in the values of $\epsilon(1)$, because of the large differences between $Z_G(1)$ and $Z_G(3)$, which have to be ascribed partly to differences between the values for C/V_G^2 .

The values of the individual terms of eq. (13), the values of ϵ_{58} , $\epsilon(1)$, $\epsilon(3)$, and the differences $\Delta \epsilon(x) = \epsilon(x) - \epsilon_{58}$, are given in table XII.

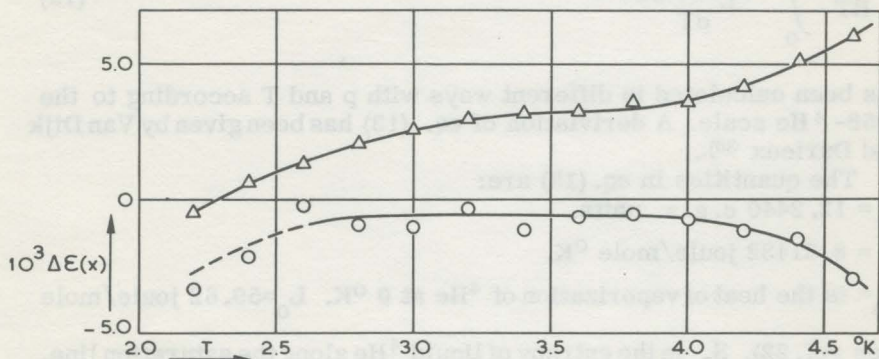


FIG. 15. Differences between the virial corrections ϵ , obtained in different ways.

$$\Delta \epsilon(x) = \epsilon(x) - \epsilon_{58}$$

ϵ_{58} calculated from eq. (13), using the 1958-⁴He scale.

$\circ \epsilon(1)$, calculated from $V_G(1)$

$\Delta \epsilon(3)$, calculated with the same virial coefficients as used for the calculation of $V_G(3)$.

The differences $\Delta \epsilon(x)$ are also shown in fig. 15. The agreement between $\epsilon(1)$ and ϵ_{58} is much better than that between $\epsilon(3)$ and ϵ_{58} .

The scattering of the $\Delta \epsilon(1)$ -values is due to irregularities in the smoothed L_a -values. The deviations from the smooth curve, however,

TABLE XII

Calculation of ϵ_{58} and comparison with $\epsilon(1)$ and $\epsilon(3)$. $\Delta\epsilon(x) = \epsilon(x) - \epsilon_{58}$. Explanation of ϵ in the text.

T_{58} $^{\circ}\text{K}$	$\frac{L_0}{RT}$	$\frac{5}{2} \ln T$	$\frac{1}{RT} \int_0^T S_L dT$	$\frac{1}{RT} \int_0^T V_L dp$	$\ln P_{58}$	ϵ_{58}	$\epsilon(1)$	$\epsilon(3)$	$\Delta\epsilon(1)$	$\Delta\epsilon(3)$
2.2	3.2594	1.9711	0.1190	0.0081	10.8958	0.0510	0.0476	0.0505	-0.0034	-0.0005
2.4	2.9878	2.1887	0.1789	0.0117	11.3433	0.0656	0.0634	0.0662	-0.0022	+0.0006
2.6	2.7580	2.3888	0.2369	0.0160	11.7358	0.0819	0.0816	0.0832	-0.0003	0.0013
2.8	2.5610	2.5740	0.2924	0.0211	12.0853	0.0996	0.0986	0.1016	-0.0010	0.0020
3.0	2.3903	2.7465	0.3460	0.0271	12.3998	0.1185	0.1174	0.1210	-0.0011	0.0025
3.2	2.2409	2.9079	0.3980	0.0341	12.6854	0.1383	0.1379	0.1413	-0.0004	0.0030
3.4	2.1090	3.0594	0.4487	0.0420	12.9470	0.1593	0.1591	0.1625	-0.0012	0.0032
3.6	1.9919	3.2023	0.4985	0.0509	13.1880	0.1812	0.1805	0.1844	-0.0007	0.0032
3.8	1.8870	3.3375	0.5477	0.0610	13.4113	0.2035	0.2029	0.2071	-0.0006	0.0036
4.0	1.7927	3.4657	0.5965	0.0722	13.6195	0.2268	0.2260	0.2304	-0.0008	0.0036
4.2	1.7073	3.5877	0.6451	0.0848	13.8145	0.2504	0.2492	0.2546	-0.0012	0.0042
4.4	1.6297	3.7040	0.6937	0.0988	13.9980	0.2746	0.2731	0.2798	-0.0015	0.0052
4.6	1.5589	3.8151	0.7431	0.1147	14.1717	0.2999	0.2969	0.3060	-0.0030	0.0061

correspond to less than 0.1 % in the L_a -values, which is within the accuracy of the L_a -values and the calculations of $\epsilon(1)$.

Above 2.5 °K the differences between $\epsilon(1)$ and ϵ_{58} may be due to uncertainties in the values of $\int_0^T S_L dT$, as in this temperature range $\Delta \epsilon(1)$ is about 0.5 % of $(1/RT) \int_0^T S_L dT$ at 2.5 °K. It decreases between 2.5 °K and 4 °K to about 0.1 % at 4 °K and it increases again to about 0.4 % at 4.6 °K.

The difference $\Delta \epsilon(1)$ between 2.5 °K and 4.2 °K can also be explained by the uncertainty in L_a , as $\Delta \epsilon(1)$ corresponds to a change of 0.07 % in L_a at 2.6 °K and of 0.12 % at 4.2 °K.

At 2.2 °K the difference between $\epsilon(1)$ and ϵ_{58} is difficult to explain from the uncertainty in $\int_0^T S_L dT$ only. When the error in $\int_0^T S_L dT$ is estimated to be 1%, the error in ϵ_{58} will be about 0.0012, whereas $\Delta \epsilon(1)$ is 0.0034 at 2.2 °K. Therefore, below 2.5 °K the uncertainties in L_a and in $\int_0^T S_L dT$ have to be taken into account to explain $\Delta \epsilon(1)$. To obtain agreement between $\epsilon(1)$ and ϵ_{58} at 2.2 °K, a change of - 1% in $\int_0^T S_L dT$ and of - 0.2 % in L_a is needed. The change in L_a of 0.2 % is somewhat larger than the estimated error, which is 0.13 % (see section 3), but as the extrapolation from the experimental L_a -values is rather difficult below 2.3 °K, a somewhat larger error at 2.2 °K cannot be excluded.

In conclusion it can be stated that the V_G -values resulting from our research, the S_L -values according to Clement ³¹⁾ and the V_L -values according to Edwards ²⁵⁾ form a practically consistent set of pVT and thermal data, when using the 1958- ⁴He scale.

To obtain agreement between ϵ_{58} and $\epsilon(3)$, keeping $\epsilon(3)$ and the 1958 - ⁴He scale unchanged, the value of $\int_0^T S_L dT$ have to be raised with 0.6 % to 0.8 % in the temperature range from 2.8 to 4.6 °K.

These changes are still within the estimated accuracy of

$\int_0^T S_L dT$. From the increase of $\int_0^T S_L dT$ the corresponding change of S_L can be estimated. In the next section it will be shown that the change in S_L , needed to make ϵ_{58} agree with $\epsilon(3)$, would enlarge the difference between the L_a -values obtained from thermodynamic calculations and the L_a -values according to table IX so much that it becomes impossible to obtain agreement between the calculated L_a -values and the experimental L_a -values, and at the same time between ϵ_{58} and $\epsilon(3)$.

10. Calculation of the heat of vaporization of ^4He from thermodynamic data

The apparent heat of vaporization has been calculated from $L_a = L + TV_L dp/dT$, in which L has been obtained from the equation

$$L = RT \left(\frac{5}{2} \ln T - \ln p + i_0 + \frac{5}{2} \right) + RT \epsilon + RT \eta - T S_L \quad (14)$$

A derivation of eq. (14) has been given by Van Dijk and Durieux³⁰⁾. The quantities in eq. (14) are the same as those in eq. (13).

$$\eta = (B - TdB/dT)/V_G + (C - \frac{1}{2} TdC/dT)/V_G^2$$

Since it is not possible to calculate η from $V_G(1)$ and $Z_G(1)$ with sufficient accuracy, the same virial coefficients have been used for the calculation of ϵ and η as for the calculation of $V_G(3)$, i. e.:

$B = (0.6824 - 17.244/T)22.427 \text{ cm}^3/\text{mole}$, and

$C = (5000/T - 4.86 \times 10^6/T^6) \text{ cm}^6/\text{mole}^2$. For the other quantities the same data have been used as for the evaluation of eq. (13).

In table XIII the values of the individual terms and the results for L_a , denoted by L_a^* , are given. In this table the term A is equal

TABLE XIII

Calculation of L_a of ^4He from thermodynamic data.								
Units of the terms: joule/mole. $\Delta L_a^* = L_a^* - L_a$.								
T °K	A	RT ϵ (3)	-RT η	TS _L	L*	TV _L $\frac{dp}{dT}$	L _a *	ΔL_a
2.2	106.439	0.929	2.216	14.216	90.94	0.78	91.92	-0.13
2.4	111.533	1.321	3.198	17.734	91.92	1.17	93.09	-0.07
2.6	116.668	1.799	4.401	21.065	93.00	1.67	94.67	+0.02
2.8	121.818	2.365	5.848	24.564	93.77	2.31	96.08	-0.12
3.0	126.977	3.018	7.559	28.344	94.09	3.10	97.19	-0.20
3.2	132.138	3.759	9.563	32.426	93.91	4.06	97.97	-0.28
3.4	137.284	4.594	11.891	36.832	93.16	5.23	98.39	-0.40
3.6	142.424	5.519	14.592	41.569	91.78	6.64	98.42	-0.50
3.8	147.552	6.543	17.723	46.668	89.70	8.31	98.01	-0.56
4.0	152.658	7.662	21.377	52.192	86.75	10.29	97.04	-0.69
4.2	157.741	8.891	25.708	58.170	82.75	12.72	95.47	-0.80

to $RT \left(\frac{5}{2} \ln T - \ln p + i_0 + \frac{5}{2} \right)$. The differences between L_a^* and L_a according to table IX, $\Delta L_a = L_a^* - L_a$, are given in the last column of table XIII. These differences are also shown in fig. 16. Below 2.7 °K the differences are within the accuracy of the measurements and of the data used for the calculation of L_a^* .

If the p-T relation, used for the calculation of L_a^* , and L_a are correct, the increasing differences above 2.7 °K are due to inaccuracies in the virial coefficients and/or in the entropy S_L .

When the virial coefficients, used for the calculation of L_a^* , are not changed, the value of $T S_L$ has to be lowered with 0.5 % at 2.8 °K

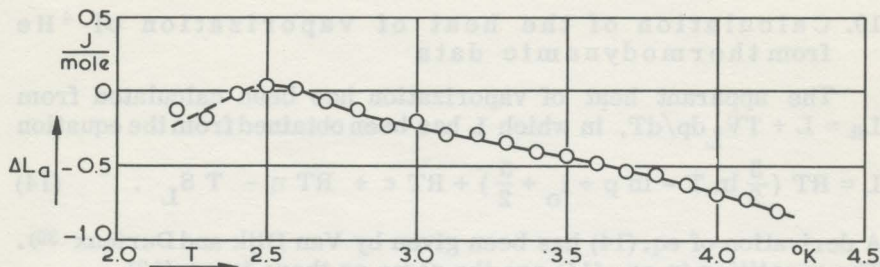


FIG. 16. Differences between L_a^* , calculated from eq.(14), and L_a according to Table IX.

Table IX.

$$\Delta L_a = L_a^* - L_a.$$

to make L_a^* agree with L_a . The change of $T S_L$ increases to about 1.4 % at 4.2 °K. Due to this change of S_L , the value of

$\int_0^T S_L dT$ decreases with about 1 % at 4.2 °K. Consequently the

value of ϵ_{58} , calculated from eq. (13) (see section 9) decreases with about 0.0012. Due to this decrease of ϵ_{58} the value of $\Delta \epsilon(3)$ at 4.2 °K increases to 0.0054.

Therefore, it is not possible to obtain agreement between L_a^* and L_a and at the same time between $\epsilon(3)$ and ϵ_{58} by keeping the p-T relation and the virial coefficients used for the calculation of L_a^* and $\epsilon(3)$ unchanged.

Unfortunately, it is not possible to estimate the value of η , when $\epsilon(1)$ instead of $\epsilon(3)$ is used for the calculation of L_a^* . However, the change in η , needed to obtain agreement between L_a^* and L_a , is only about 3 % of the value of η , which is within the accuracy of the available data for B, C, dB/dT and dC/dT .

11. Concluding remarks

The discussions given in this chapter show that agreement between the 1958-⁴He scale and the thermodynamic p-T relation according to eq. (13) can be obtained within the accuracy of the available data needed for the evaluation of eq. (13).

However, the uncertainty in the available pVT and thermal data allow changes in the thermodynamic p-T relation of several millidegrees, especially above 4.2 °K.

To test the accuracy of the 1958-⁴He scale in this temperature range accurately by thermodynamic calculations, using eq. (13), more accurate data about the specific heat, the heat of vaporization at 0 °K and the virial coefficients of ⁴He are needed.

If Clapeyron's equation is used to evaluate the thermodynamic p-T relation, the measurements can be restricted to the determination of L_a and V_G as functions of the pressure, since Clapeyron's equation can be written as

$$\frac{d \ln T}{dp} = \frac{V_G(p)}{L_a(p)} \quad (15)$$

If one point of the p-T relation, eq. the normal boiling point, is known, an accurate p-T relation can be derived from eq. (15), when $V_G(p)$ and $L_a(p)$ have been measured accurately.

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SAMENVATTING

De verdampingswarmten van waterstof en van helium zijn niet alleen belangrijk als thermodynamische grootheden van de in de lage-temperatuurphysica meest gebruikte vloeibaar gemaakte gassen, maar ook voor de afleiding van dampspanningsrelaties (p-T relaties), die gebruikt worden voor het meten van de temperatuur in het gebied van vloeibare waterstof en van vloeibaar helium.

De verdampingswarmte is op een eenvoudige wijze verbonden met de afgeleide naar de temperatuur van de druk van de verzadigde damp door de vergelijking van Clapeyron, die kan worden geschreven als $dp/dT = L_a/TV_G$ of als

$$d \ln p/dT = L_a / \left\{ RT^2 (1 + B/V_G + C/V_G^2) \right\}$$

Indien de schijnbare verdampingswarmte L_a , de viriaalcoëfficiënten B en C van de toestandsvergelijking $pV = RT (1 + B/V_G + C/V_G^2)$ en één punt van de p-T relatie (b. v. het kookpunt) bekend zijn, kan de p-T relatie worden berekend. V_G is het molaire volume van de verzadigde damp.

Is de dampspanningsrelatie reeds met voldoende nauwkeurigheid bekend, dan kunnen nauwkeurige gegevens voor de verdampingswarmte worden gebruikt om de consistentie van de V_G -waarden berekend met de gegevens voor de viriaalcoëfficiënten en de V_G -waarden berekend met behulp van de dampspanningsrelatie te toetsen.

In hoofdstuk II van dit proefschrift wordt de apparatuur voor de metingen van de schijnbare verdampingswarmte van waterstof en van helium beschreven.

In hoofdstuk III worden de resultaten voor evenwichtswaterstof vermeld. Met deze resultaten en bekende gegevens voor de viriaalcoëfficiënten werd een p-T relatie berekend. Goede overeenkomst werd gevonden met de p-T relatie, afgeleid uit de magnetische-temperatuurmetingen van Durieux (de T_{L60} -schaal) en met de magnetische-temperatuurmetingen van Van Rijn.

Ook werden nauwkeurige metingen verricht van de tripelpuntsdruk van evenwichtswaterstof. De gevonden waarde, $p_{tr} = 52.73 + 0.01$ mm Hg, 0°C is in zeer goede overeenstemming met de resultaten van Muijlwijk, Durieux en Van Dijk, die, gebruik makende van andere apparatuur, dezelfde waarde vonden. In de uit L_a berekende p-T relatie komt deze druk overeen met een temperatuur van 13.802°K . De nauwkeurigheid van deze tripelpuntstemperatuur wordt geschat op 0.006°K ten opzichte van een vaste waarde voor het normale kookpunt van waterstof.

In hoofdstuk IV worden de resultaten van de metingen van de verdampingswarmte van ^4He vermeld. Deze resultaten werden gebruikt om het molaire volume, V_G , van de verzadigde damp van helium te berekenen. Ook werd V_G berekend met de toestandsvergelijking $pV_G = RT (1 + B/V_G + C/V_G^2)$, waarin p en T overeenkomstig de

1958 - ^4He schaal werden genomen en voor de viriaalcoëfficiënten B en C bekende gegevens werden gebruikt. Beneden 4.2°K werd binnen de nauwkeurigheid waarmee de p-T relatie en de viriaalcoëfficiënten bekend zijn, overeenstemming tussen de beide series V_G -waarden gevonden. De verschillen, gevonden boven 4.2°K , moeten worden toegeschreven aan het gebruik van slechts de tweede en de derde viriaalcoëfficiënt in de toestandsvergelijking.

1938 - De schaal werden genomen op voor de vriescoëfficiënten
B en C bekende gegevens worden gebruikt. Bandoen 4.2 °K werd
drukt de nauwkeurigheid waarmee de p-T relatie en de vriesco-
ëfficiënten bepaald zijn, overeenstemming tussen de beide series
V₁ werden gevonden. De verschillen, gevonden boven 4.2 °K,
moeten worden toegeschreven aan het gebruik van slechts de twee
de en de derde vriescoëfficiënt in de toestandsvergelijking.



STELLINGEN

I

De langs thermodynamische weg berekende p-T relatie voor evenwichtswaterstof en die afgeleid uit magnetische temperatuurmetingen wijzen er beide op, dat 13,809°K voor de tripelpuntstemperatuur, indien men het kookpunt vaststelt op 20,268°K, te hoog is.

Vergadering van de Werkgroep II van het Comité Consultatif de Thermométrie, Moskou, 1966.
Dit proefschrift, hoofdstuk III, 4a.

II

Het verdient aanbeveling te onderzoeken of een dampspanningsthermometer waarin zich vaste waterstof bevindt, kan worden gebruikt voor nauwkeurige temperatuurmetingen in het gebied van 10°K tot 14°K.

III

De verschillen tussen de resultaten van de temperatuurmetingen met de acoustische interferometer door Plumb en Cataland, en de 1958-⁴He temperatuurschaal maken een nadere nauwkeurige bepaling van het kookpunt van helium met de gasthermometer gewenst.

H.H. Plumb and G. Cataland, Science 150 (1965) no. 3693, p. 155.

IV

Zolang niet is aangetoond dat de door Lovejoy voorgestelde berekening van gereduceerde weerstandsverschillen voor platina thermometers bij -78.5°K met de relatie van Callendar en Van Dusen betere overeenstemming met de gevonden gereduceerde weerstandsverschillen oplevert dan de berekeningsmethode die gebaseerd is op de wet van Matthiesen, verdient deze laatste methode de voorkeur.

Vergadering van de Werkgroep II van het Comité Consultatif de Thermométrie, Moskou, 1966:
D.R. Lovejoy, Document No. 4A.
M. Durieux, H. van Dijk en R. Muijlwijk, Document No. 25.

V

In de door Meincke gegeven berekening van het potentiaalverschil tussen twee punten van een in een bewegend magnetisch veld geplaatst preparaat waarvan de weerstand afhankelijk is van het magnetische veld, is de invloed van de scalaire potentiaal ten onrechte verwaarloosd.

P.P.M. Meincke, Phys. Rev. Letters 17 (1966) 390.

VI

Er zijn bezwaren aan te voeren tegen de afhankelijkheid van de polariseerbaarheid van het ^3He -atoom van de dichtheid zoals die is voorgesteld door Kerr en Sherman.

E.C. Kerr and R.H. Sherman, 10th. Internat. Conf. on Low Temp. Phys., Moskou, 1966, Document H 45.

VII

De conclusie van Jaclevic e. a., dat de resultaten van hun metingen aan twee parallelle Josephson-contacten een overtuigende bevestiging vormen van het Aharonov-Bohm effect, is niet juist.

R.C. Jaclevic, J. Lambe, J.E. Mercereau and A.H. Silver, Phys. Rev. 140 (1965) A 1628.

VIII

Er is alle aanleiding om de door De Vries gevonden waarden voor de magnetische term in de soortelijke warmte van koperkaliumchloride ($\text{CuK}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$) te vergelijken met de daarvan afwijkende resultaten van Van den Broek en van Van Kempen.

A.J. de Vries, proefschrift, Leiden, 1965, p. 103.

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H. van Kempen, proefschrift, Leiden, 1965, p. 47.

IX

Voor temperatuurmetingen in het temperatuurgebied van -183°C tot 100°C is het gebruik van thermo-elementen in veel gevallen te verkiezen boven het gebruik van vloeistof-in-glas thermometers.

X

Met het oog op de ijking van germanium thermometers tussen 5°K en 14°K is het wenselijk de reproduceerbaarheid van enkele vaste punten in dit temperatuurgebied nader te onderzoeken.

H. ter Harmsel, 21 december 1966.

