THERMOMETRY AT LIQUID HELIUM AND LIQUID HYDROGEN TEMPERATURES

M. DURIEUX

STELLINGEN

1. De relatie tussen de dampspanning van vloeibaar ^{3}He en de temperatuur (p-T-relatie) is voor lage temperaturen gebaseerd op magnetische temperatuurbepalingen. Afwijkingen van de wet van Curie voor de gebruikte paramagnetische zouten zullen de verkregen p-T-relatie beïnvloeden. Het verdient aanbeveling dit nader te onderzoeken.

2. Bij de nauwkeurige bepaling van de susceptibiliteit als functie van de temperatuur van een in een spoelensysteem geplaatst preparaat, door meting van de wederkerige inductie van die spoelen, kunnen effecten van de lege spoelen van grote invloed zijn.

3. Hoare en Zimmerman vonden dat de temperatuur in hun dampspanningsthermometer opliep als de stookstroom in de heliumkryostaat verminderd werd. Dit wijst er op, dat er een aanzienlijke warmtetoevoer van buitenaf naar het reservoir van de dampspanningsthermometer bestond.

   Hoare, F.H. and Zimmerman, J.E., Rev. sci. Instrum. 39 (1959) 184.

4. Informatie over de viriaalcoëfficiënten van waterstofgas in het temperatuurgebied van vloeibare waterstof kan worden verkregen uit nauwkeurige metingen van de dampspanning en de verdampingswarmte van vloeibare waterstof als functie van de temperatuur.

5. Berman en Mate gebruikten bij hun berekening van de dichtheid van de verzadigde damp van vloeibaar helium tussen 2,2 en 3,0°K de tweede viriaalcoëfficiënt zoals deze door Kilpatrick, Keller en Hammel is gegeven. Een nadere analyse wijst uit dat er bij 2,5°K nog een invloed van 3°/oo is op de berekende dichtheid tengevolge van de derde viriaalcoëfficiënt.

   Berman, R. and Mate, C.F., Phil. Mag.3 (1958) 461.
   Kilpatrick, J.E., Keller, W.E. and Hammel, E.F., Phys. Rev. 97 (1955) 9.

M.Durieux

6. Voor mangaanammoniumsulfaat bestaat er geen overeenstemming tussen de resultaten van Bleaney en Ingram en van Miedema e.a. wat betreft het teken van de kristalveldsplitsing. Voor dit zout, en ook in soortgelijke gevallen, kunnen nauwkeurige metingen van de susceptibiliteit van monokristallen als functie van de temperatuur tussen 20 en 1°K van nut zijn voor de bepaling van de grootte en het teken van de kristalveldsplitsingen.

Bleaney, B. and Ingram, D.J.E., Proc. roy. Soc. A 205 (1951) 336.
Miedema, A.R., Van den Broek, J., Postma, H. and Huiskamp, W.J., Commun. Leiden No. 318a; Physica 25 (1959) 1177.

7. Het moet verwondering wekken dat er tot nu toe geen tegenspraak gevonden is tussen experiment en isobaar-model bij de π, 2π-verstrooiing, gezien de beschrijving met niet-symmetrische golffuncties ten aanzien van de twee uitgaande π-mesonen, die bij dit model gebruikt wordt.

8. Recente metingen van resonantiefluorescentie van gammastralen (Mössbauer-effect) hebben aangetoond, dat men door relatieve beweging van bron en resonantieverstrooier informatie kan verkrijgen over de hyperfijnstruktuur van aangeslagen toestanden van atoomkernen in vaste stoffen. In bepaalde gevallen zou men door meting van de circulaire polarisatie van de gammastraling ook het teken van het magnetisch moment van de aangeslagen toestand kunnen vaststellen.

DePasquali, G., Frauenfelder, H., Margulies, S. and Peacock, R.N., Phys. Rev. Letters 4 (1960) 71.

9. Het is theoretisch aannemelijk dat de restweerstand van zeer zuiver ijzer toeneemt bij verdere zuivering.

10. De kernspinecho-methode kan gebruikt worden om de samenstelling te bepalen van mengsels zoals ortho H_2-para H_2, ortho D_2-para D_2 en H_2-D_2.

11. De bewering van Atkins, dat de door Wansink en Taconis gemeten lage waarde voor de viscositeit van vloeibare ^{3}He-^{4}He mengsels in nauwe spleten bij 1,2°K aan een effect van de vrije weglengte van de phononen te wijten zou zijn, is onjuist.

Atkins, K.R., Liquid helium (Cambridge Univ. Press, 1959) p.291.

12. De verklaring die Sharpe geeft van de door hem gevonden afhankelijkheid van de omzettingssnelheid van ergosterol in vitamine D_2 van het oplosmiddel, is aan bedenkingen onderhevig.

p. 46 Sharpe, L.H., Thesis Michigan (1957).

13. Het meten van temperatuurverschillen met een nauwkeurigheid van een duizendste graad met een z.g. ultra-beckmannthermometer vereist reeds bijzondere voorzorgen; een hogere nauwkeurigheid is niet te verwachten.

RECEPTIE NA AFLOOP DER
PROMOTIE IN HET UNIVERSITEITSGEBOUW

THERMOMETRY AT LIQUID HELIUM AND LIQUID HYDROGEN TEMPERATURES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT
TE LEIDEN OP GEZAG VAN DE RECTOR MAGNIFICUS
Mr. J. E. JONKERS, HOOGLERAAR IN DE FACULTEIT DER
RECHTSGELEERDHEID, PUBLIEK TE VERDEDIGEN
OP WOENSDAG 16 MAART 1960 TE 14 UUR

DOOR

MARTEN DURIEUX

GEBOREN TE KATWIJK IN 1926

DRUCO DRUKKERIJ BEDRIJVEN - LEIDEN

Promotor: Prof.Dr C.J. Gorter

Dit proefschrift is bewerkt onder toezicht van Dr H. van Dijk

Aan mijn Ouders

Promotor: Prof.Dr C.J. Gorter

Het proefschrift is bewerkt onder toezicht van Dr H. van Dijk

Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hier enkele gegevens betreffende mijn studie.
Na het doorlopen van de Chr. Muloschool te Katwijk werd ik in 1942 toegelaten tot de Chr. H.B.S. (thans Lyceum) te Leiden, waar ik in 1944 het eindexamen B aflegde.
In 1945 begon ik mijn studie in de Faculteit der Wis- en Natuurkunde. Het candidaatsexamen e werd in 1950 afgelegd en het doctoraalexamen experimentele natuurkunde in 1955. De tentamina voor het doctoraal examen werden afgenomen door Dr J. Korringa, Dr N.G. van Kampen en Prof. Dr C.J.F. Böttcher.
Inmiddels was ik sinds december 1950 werkzaam op het Kamerlingh Onnes Laboratorium. Het eerste halfjaar assisteerde ik Dr C.C. Vlam bij een onderzoek over fluorescentie van anorganische phosphoren, daarna kwam ik op de afdeling Thermometrie, die onder leiding staat van Dr H. van Dijk. Hier werkte ik eerst aan verschillende onderzoeken op het gebied van de thermometrie, later werd mijn speciale opdracht het doen van magnetische temperatuurmetingen ter vastlegging van de temperatuurschaal in het temperatuurgebied van vloeibaar helium.
Gedurende de jaren 1952 tot 1954 was ik als assistent verbonden aan het practicum voor praecandidaten. Vanaf 1954 verzorgde ik de "Communications from the Kamerlingh Onnes Laboratory of the University of Leiden" als opvolger van Dr W. Tuyn. In 1959 werd ik benoemd tot wetenschappelijk ambtenaar 1e klasse.
De in dit proefschrift vermelde onderzoekingen werden verricht onder leiding van Dr H. van Dijk. In het beginstadium van het onderzoek werkten hieraan mede de heren B. Knook, H.A. Wedding en A. van Vegten, Mej. O.P. van Wier, en de heren F.J. Du Chatenier, D.G. Kapadnis en L. Pals. De experimenten, die in dit proefschrift beschreven zijn, zijn gedaan met medewerking van de heren H. ter Harmsel, C. Steendam en C. van Rijn. Van groot belang voor het uitvoeren van de metingen was dat Dr L.C. van der Marel en de heer J. van den Broek ons hun meetbrug ter beschikking stelden. Alle in dit proefschrift beschreven wederkerige inductie-metingen zijn hiermee uitgevoerd. Bij het tot stand komen van de berekeningen in Hoofdstuk IV had ik de hulp van de heer A.R. Miedema.
Behalve van de wetenschappelijke staf ondervond ik veel steun van de technische en administratieve staf van het Kamerlingh Onnes Laboratorium. In het bijzonder noem ik de heren A. Ouwerkerk, J.A.Th. van Schooten en T. Nieboer, die de onderzoekingen cryogeen technisch verzorgden en de heer H. Kuipers, die de glasapparatuur vervaardigde. De verzorging van de Communications geschiedde vanaf 1957 in samenwerking met Mej. C. Kesseboom.

De engelse tekst van dit proefschrift werd gecorrigeerd door de heer C. M. Knobler.

CONTENTS

page

Chapter I

INTRODUCTION

Chapter II

MAGNETIC MEASUREMENTS OF THE VAPOUR PRESSURE-TEMPERATURE RELATIONS OF LIQUID ^{4}He AND H_2

Chapter III

THE VAPOUR PRESSURE-TEMPERATURE RELATION OF LIQUID ^{4}He

Chapter IV

COMPARISON OF MAGNETIC TEMPERATURES WITH T_{58}. THE WEISS CONSTANT

CHAPTER I

INTRODUCTION

The vapour pressure-temperature relations for liquid helium and liquid hydrogen have been the subject of many investigations since these relations are used as secondary standards for temperature measurements. A milestone was reached with the adoption of the 1958 ^{4}He Scale of Temperatures by the International Committee on Weights and Measures in October 1958. This scale was the result of international cooperation. For hydrogen there is as yet no official vapour pressure temperature scale although several scales have been in use.

In this thesis the vapour pressure-temperature relations for liquid helium and liquid hydrogen are discussed with particular emphasis on the measurements with a magnetic thermometer made at the Kamerlingh Onnes Laboratory. Magnetic temperature measurements involve the determination of the susceptibility of paramagnetic salts obeying Curie's law to a good approximation. Our susceptibility measurements, which had to be very accurate, revealed small deviations from Curie's law for potassium chromium alum and methylammonium chromium alum which had not been found before. The discussion of the hydrogen vapour pressure-temperature relation leads to the proposal of a new vapour pressure temperature scale which differs slightly from those now in use. The technique of temperature measurements using the vapour pressure is another subject of this thesis. A few introductory remarks will be made.

The thermodynamic temperature scale

The thermodynamic temperature scale was introduced by Kelvin in 1848. The size of the degree on this scale was last fixed at the Tenth General Conference on Weights and Measures in 1954 by adopting the value 273.16 exactly for the triple point of water [1] according to the recommendation of the Advisory Committee on Thermometry [2].

The Advisory Committee on Thermometry to the International Committee on Weights and Measures meets in Sèvres, near Paris (lastly in 1958) and gives recommendations for international arrangements in the field of thermometry. They are subject to approval by the International Committee on Weights and Measures and finally by the General Conference on Weights and Measures which meets usually every six years in Sèvres (lastly in 1954).

Over a large range of temperatures, the thermodynamic temperature can be measured with a gas thermometer [3,4]. The procedure is in principle the following:

A bulb containing a known amount of gas is brought into contact with the system whose temperature T is desired. The quantity pV/N is determined, where p is the pressure of the gas, V the volume of the bulb and N the number of moles of the gas within. This is done for different amounts of gas in the bulb and $\lim_{N\to 0} pV/N$ is determined. The experiment is repeated with the bulb at the temperature of water at its triple point; this results in a value $(\lim_{N\to 0} pV/N)_{\mathrm{tr.point}}$. The thermodynamic temperature of the original system is then found from the relation:

$$T = \frac{\lim_{N\to 0} pV/N}{(\lim_{N\to 0} pV/N)_{\mathrm{tr.point}}} \times 273.16^{\circ}\mathrm{K} \qquad (1)$$

When the virial coefficients of the gas are known, measurements using a constant amount of gas in the gas thermometer are sufficient.

Measurements with the gas thermometer have been made from the melting point of gold 1063°C (occasionally up to 1550°C) [5] down to 1.2°K. At the lower temperatures a limit is set by the fact that no gas is available with a sufficiently high pressure to permit a reasonable accuracy in the measurements.

Temperature measurements between 20.4 and 1°K

Measurements with the gas thermometer are elaborate and not as sensitive as is sometimes desired. Therefore practical temperature scales are in use. The vapour pressure scale of liquid ^{4}He is mostly used for temperature measurements between the boiling point of helium (4.2150°K) and about 1.0°K and it can be used up to the critical point of helium (p = 1718 mm Hg, 0°C *), T = 5.1994°K). Below 1.2°K the vapour pressure becomes so small that it is difficult to obtain an accuracy of 1 m°K in the temperature by measuring the vapour pressure. In 1955 two vapour pressure temperature scales for helium were proposed to replace the 1948 scale [6], one called the T_{55E} scale [7] and the other the T_{L55} scale [8]. The use of two different scales was very unsatisfactory and, as mentioned, they were replaced in 1958 by the 1958 scale [9].

---

* The pressure unit mm Hg, 0°C means throughout this thesis mm Hg at 0°C and standard gravity (g = 980.665 cm/s^2), this unit is equal to (1/760) x 1013250 dynes/cm^2.

Figs. 1a and b show two methods for determining the temperature from the vapour pressure. The first method yields only the temperature at the surface of the liquid bath. The second method employs a separate vapour pressure thermometer, consisting of a bulb in which a small amount of liquid is condensed and a tube connecting the bulb to the manometer. The second method is usually employed for more accurate temperature measurements.

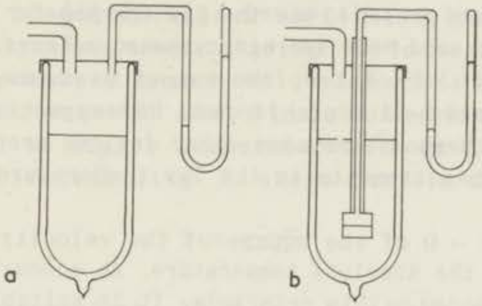

Fig. 1

Temperature measurements using the vapour pressure of liquid helium or hydrogen.
a. Measurement of the bath pressure. b. Vapour pressure thermometer.

The normal region for the use of the vapour pressure of hydrogen for temperature measurements is between about 20.4 and 14°K. A complication is the occurrence of the ortho and para forms of hydrogen. The H_2 molecule occurs in two forms: in the ortho form the spins of the protons are parallel to each other, in the para form they are opposite to each other. The thermodynamic properties of ortho and para hydrogen differ somewhat since the molecules are in different rotational states[10]. The difference between the boiling points is 0.118°K. The equilibrium composition at high temperatures (room temperature) is 75% ortho-H_2 and 25% para-H_2, and at 20.4°K 99.79% para-H_2 and 0.21% ortho-H_2. Hydrogen having the composition 75% o-H_2 and 25% p-H_2 is generally called "normal hydrogen" and hydrogen having the composition 99.79% p-H_2 and 0.21% o-H_2 "20.4°K equilibrium hydrogen" or "equilibrium hydrogen". Freshly liquefied pure normal hydrogen changes its vapour pressure at a rate of about 0.3 mm Hg per hour. Recently catalysts have become available by which small amounts of equilibrium hydrogen to be used in a vapour pressure thermometer can readily be prepared.

Temperature measurements using the vapour pressure have the advantage of being perfectly reproducible. However they are not very convenient for such experiments as specific heat and heat conductivity measurements. Therefore resistance thermometers of several kinds have been developed for the low temperature region such as phosphorbronze thermometers, carbon thermometers and germanium thermometers. They are usually calibrated against the vapour pressures of helium and hydrogen and, occasionally, between 4.2°K (or 5.2°K) and 14°K against the gas thermometer. Some investigators prefer to use the gas thermometer also between 14 and 20.4°K instead of the hydrogen vapour pressure thermometer. Besides the gas thermometer, the vapour pressure thermometer filled with liquid helium or hydrogen, the magnetic thermometer and resistance thermometers some other devices used or proposed for temperature measurements in the low temperature region will be mentioned.

The limit for $p \to 0$ of the square of the velocity of sound is proportional to the absolute temperature. An accoustical thermometer has been based on this principle. It is suitable for direct measurements of the thermodynamic temperature. As yet its accuracy is less than that of the gas thermometer [11, 12], but new investigations have been announced [13]. Temperature measurements using the thermal noise of a resistance have not given sufficient accuracy. The ^{3}He vapour pressure thermometer is used as a secondary standard in measurements with ^{3}He [14, 15].

Summary of contents

In Chapter II the method and the results of magnetic temperature measurements of the vapour pressure-temperature relation of liquid helium and hydrogen are presented. The results obtained for the ^{4}He region are compared with T_{L55} and T_{55E}. In Chapter III the vapour pressure-temperature relation for liquid helium is treated. In Chapter IV the results of the measurements described in Chapter II are compared with the new helium vapour pressure temperature scale T_{58}. Moreover, some measurements of the Weiss constants of potassium chromium alum and methylammonium chromium alum are given and the theoretical equations for the susceptibility of these salts are discussed. Chapter V deals with the vapour pressure-temperature relation for liquid hydrogen. In Chapter VI the technique of temperature measurements using the vapour pressure of helium is discussed. Experimental results of measurements of the temperature gradient in a liquid helium bath are presented and compared with results obtained by others.

CHAPTER II

MAGNETIC MEASUREMENTS OF THE VAPOUR PRESSURE-TEMPERATURE RELATIONS OF LIQUID ^{4}He AND H_2

1. Introduction

1a. Principle of the method

The method of determining temperatures by measuring the susceptibility of a paramagnetic salt has been used extensively in the temperature region below 1°K. In 1936, Professor E.C. Wiersma suggested that it might be possible to extend this method to higher temperatures[16]. In the most simple case the susceptibility χ obeys Curie's law

$$\chi = C/T$$

where C is a constant. If χ can be measured the "magnetic thermometer" has only to be calibrated at one fixed point to determine the constant C. The sensitivity $d\chi/dT$ is proportional to T^{-2} which makes the magnetic thermometer less sensitive at higher temperatures.

Up to now all actual magnetic temperature measurements have been performed with a sample of a paramagnetic salt placed within a set of coils forming a mutual inductance or within a single coil whose self inductance can be measured. When the sample is ellipsoidal and it is placed in a region where the field of the primary coil is homogeneous, the magnetic flux ϕ through the secondary coil of such a mutual inductance due to a primary current can be written as

$$\phi = \phi_0 + bM \qquad (1)$$

where ϕ_0 is the flux through the secondary coil in the absence of the salt, M the magnetization of the salt and b a constant depending on the dimensions of the coils and the salt. The coefficient of mutual inductance L_{12} equals ϕ / i_p where i_p denotes the primary current. When H_0 is the field of the primary coil in the homogeneous region in the absence of the salt

$$L_{12} = a' + b' M/H_0 \qquad (2)$$

The quantity M/H_0 is a property of the salt; it is usually found with a good accuracy that, in agreement with the Curie Weiss law

$$M/H_0 = c_1 + c_2 / (T + \Delta) \tag{3}$$

in which c_1, c_2 and Δ are constants. One obtains

$$L_{12} = c_1' + c_2' / (T + \Delta) \tag{4}$$

The coefficient of mutual inductance can be measured with a Hartshorn mutual inductance bridge. It is usually expressed in terms of the number of turns n of a variable mutual inductance that compensates the inductance to be measured

$$n = \alpha + \beta L_{12} \tag{5}$$

One finally obtains for the relation between the measured number of turns n and the temperature

$$n = A + B / (T + \Delta) \tag{6}$$

In Chapter IV some remarks will be made on the validity of eq. (3) for some special salts.
When the self inductance method is used the self inductance can be measured with an Anderson self inductance bridge. The measured quantity in this case is a resistance R which is related to the self inductance of the coil by a linear equation similar to (5). One obtains in this case

$$R = A' + B' / (T + \Delta) \tag{7}$$

in which A' and B' are again constants.
The constant Δ in eqs. (6) and (7) is a property of the salt sample. The constants A and B in eq. (6) or A' and B' in eq. (7) depend on the salt sample and on the dimensions of the coils as well as on the bridge with which the inductance is measured.
The constants A and B (or A', B') cannot be calculated with the desired accuracy and in most cases Δ is also unknown. Thus absolute temperature measurements with the magnetic thermometer are limited by the three constants in eq. (6) or

(7) which must be determined by calibrations at at least three known temperatures.

Extensive discussions on magnetic thermometry have been given by De Klerk [17] and by Van Dijk [18].

1b. Measurements for the determination of the helium vapour pressure temperature scale

Magnetic temperature measurements have been a tool in determining the pT relation for liquid helium. The measurements involve the simultaneous determination of the susceptibility of the paramagnetic salt (actually the determination of n or R) and the saturated vapour pressure of liquid helium having the same temperature as the salt. Early measurements were made by Casimir, De Klerk and Polder [19] and by Bleaney and Hull [20]. Later on magnetic measurements were performed by Erickson and Roberts [21] and by Van Dijk and coworkers to investigate errors in the 1948 temperature scale, which were found earlier by Kistemaker in another way [22, 23]. Erickson and Roberts determined the constant A (eq. (6)) by a calibration at a relatively high temperature i.e. the boiling point of liquid nitrogen (77°K) and found that it was not possible to represent the relation between n and T in the helium region by eq. (6) when T was obtained from the saturated vapour pressure of liquid helium using T_{48}. They used as salts $Mn(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ (powder) and $Fe(NH_4)(SO_4)_2 \cdot 12\,H_2O$ (powder) and found the same deviations from eq. (6) for both salts. These could be explained by errors in T_{48} which were in general consistent with Kistemaker's results.

Measurements by Ambler and Hudson [24, 25] were made at the time that the two helium vapour pressure temperature scales T_{55E} and T_{L55} came into use. Provisional results were obtained by De Klerk and Hudson in 1953 [26]. A sphere of methylammonium chromium alum was used for which it was assumed on the basis of specific heat measurements and measurements below 1°K that $\Delta = 0$. Measurements were made only in the helium region. Preliminary results were more in agreement with T_{L55} than with T_{55E} [24] but Ambler and Hudson's final conclusion expressed a slight preference for T_{55E} over T_{L55} although the measurements were not accurate enough to resolve with certainty the discrepancy between the two scales [25].

Besides the measurement of the mutual inductance the determination of the saturated vapour pressure of the liquid in thermal contact with the salt is of great importance. In the first measurements of Erickson and Roberts the vapour pressure was measured at the top of the cryostat. In the later experiments of Erickson and Roberts and also in those of Ambler and Hudson a small amount of helium was condensed in a closed tube containing the salt and the vapour pressure of this helium was measured. Ambler and Hudson reported that the reason why they could not decide between the two scales was because of the possibility of inaccuracies in measuring the vapour pressure of the liquid in thermal equilibrium with the salt. One may note that the coils of the mutual inductance used by Erickson and Roberts were mounted outside the helium dewar in the liquid nitrogen bath, whereas in the experiment of Ambler and Hudson they were placed inside the helium dewar. The procedure of Erickson and Roberts has the advantage that a calibration can be made with the salt at the nitrogen boiling point. This is very difficult when the coils are placed inside the helium dewar since the measured mutual inductance depends also on the dimensions and on the resistance of the coils and these change with temperature. On the other hand when the coils are placed in the helium dewar it is easier to obtain a rigid construction of the salt and the coils.

In Leiden new measurements to check the helium vapour pressure temperature scale were started in 1949 by Van Dijk. At first the self inductance method was chosen because a self inductance bridge was available and it seemed worthwhile to investigate the merits of this method. Preliminary results showing errors in T_{48} in accordance with those found by Kistemaker were obtained in 1949 and shown at the Conference on Low Temperature Physics in Cambridge (Mass.) [18]. The measurements were later extended and presented at the Conference on Low Temperature Physics in Houston (1953) [27] and on the Third Symposium on Temperature in Washington (1954) [18].

1c. *Present measurements by the mutual inductance method*

In 1955 when T_{55E} and T_{L55} came into use we tried to improve our measurements. We had three aims: 1) to decide between T_{55E} and T_{L55} and to detect possible errors in these scales, especially between 4.2 and 5.2°K where the data on which the scales were based were rather scarce, 2) to get a general idea of the accuracy of magnetic thermometry at higher temperatures,

3) to check the reproducibility of temperature measurements made from the vapour pressure of liquid helium.

For the susceptibility measurements the mutual inductance method was chosen. The Hartshorn bridge used was built by L.C. van der Marel and J. van den Broek of the Kamerlingh Onnes Laboratory and used by them for their measurements on paramagnetic relaxation.

Because it was essential to insure a fixed relative position of the salt and the measuring coils, the coils were placed in the helium dewar. This did not influence measurements made at hydrogen temperatures appreciably since the change in resistance and dimensions of the coils below 20°K is very small. The salts chosen were manganese ammonium tuttonsalt ($Mn\ (NH_4)_2\ (SO_4)_2.6H_2O$) and potassium chromium alum ($K\ Cr\ (SO_4)_2.12\ H_2O$). The samples were spherically ground single crystals. Measurements were made from 1.3 to 5.2°K and from 14 to 23°K.

2. General description of the apparatus

The low temperature part of the apparatus is sketched in fig. 2. The primary coil C_p and the secondary coils C_{S1}, C_{S2} and C_{S3} formed a mutual inductance. The paramagnetic salt S was placed at the centre of the coil C_{S1}. Helium or hydrogen could be condensed in the thermometer vessel Th which was closed at its lower end by the ground plug P which carried the salt (the plug P was filled with air). The tube C connected Th to the filling and manometer system; it had a constriction Q at its lower end. Usually a small amount of liquid was also condensed in the jacket J. This jacket was connected to the manometers by the tube E which surrounded the tube C over its whole length in the cryostat. The whole apparatus was suspended from the top of the cryostat by the tube E. The outer tubes G and H served to carry the primary coil. The somewhat elastic connection F between E and G was made to make the construction more rigid. At several places some small holes were made in the tubes serving to support the coils, so that the liquid helium in the dewar could flow around them. Black paper was wrapped around the tube H above the coil. The inner walls of E and J and the outside of C were silvered. Black paper was also glued to the bottom of P. The salt could easily be removed by applying an overpressure in Th. A heater was placed at the bottom of the dewar. It consisted of a mica plate, around which a constantan wire of 56 Ω was wound.

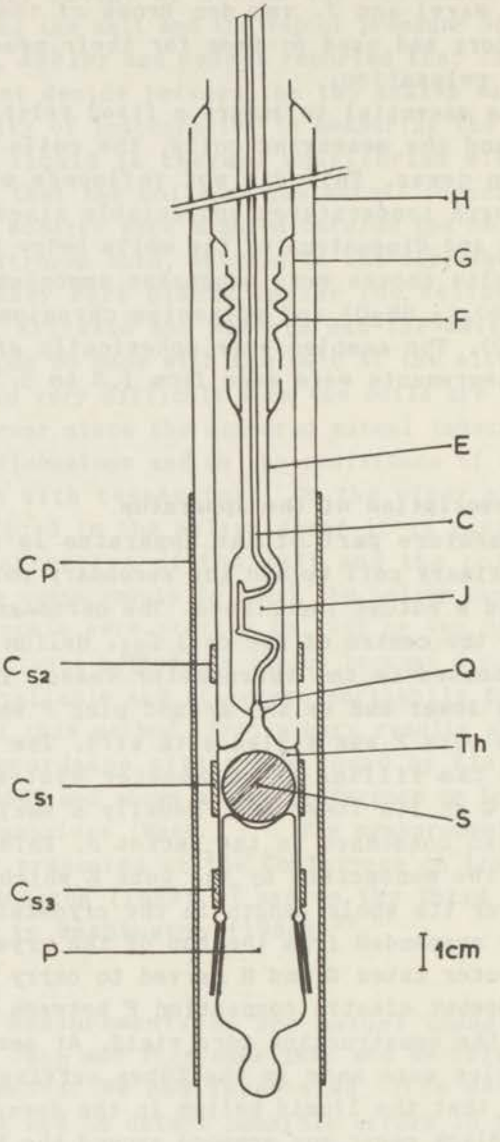

Fig. 2
Apparatus for magnetic thermometry.

The whole assembly was mounted in a silvered dewar with two unsilvered slits of 4 mm opposite each other. The length of the dewar was 1 m and its inner diameter 48 mm. The lower end of the tube H was about 4 cm above the bottom of the dewar. The helium dewar was surrounded by a second dewar filled with liquid nitrogen. During the measurements the nitrogen level was kept at about 60 cm above the bottom of the helium dewar. Liquid nitrogen was used instead of liquid air, which is usually used in this laboratory, because of the paramagnetism of oxygen which might have influenced the inductance of the coils.

The pressures in Th, J and over the helium bath were measured with a manometer system that will be described in detail later on.

As we wished to extend the measurements to the critical point of helium, the construction of the cryostat was made such that it could stand an overpressure of 1.5 atmosphere. Under the helium dewar there was a metal cup connected by means of metal strips to the cap. Cotton adhesive tape was wrapped around the rubber band connecting cap and dewar. The stopcocks that had to stand overpressure were provided with phosphorbronze springs and greased with heavy grease. The distance from the cryostat to the liquefier being only 2 meter the cryostat could be filled with a glass siphon directly from the liquefier. The vacuum in the helium dewar was pumped before every measuring day with a high vacuum pump.

Some more details of the apparatus will be discussed in the next sections.

3. The susceptibility measurement

3a. General remarks

For an estimate of the sensitivity of the susceptibility measurements the coefficient of mutual inductance L_{S1} of the middle secondary coil C_{S1} with respect to the primary coil may be written as

$$L_{S1} = L_{S1}^{o} \, (1 + 4 \pi f \chi) . \qquad (8)$$

in which L_{S1}^{o} is the mutual inductance of the empty coil C_{S1} with respect to Cp and f the effective filling factor of the coil system.

For manganese ammonium tuttonsalt

$$L_{S1} = L_{S1}^{o}\ (1 + 0.26\ f/T)$$

and

$$dL_{S1}/dT = -\ L_{S1}^{o} \times 0.26\ f/T^2 \qquad (9)$$

and for potassium chromium alum

$$L_{S1} = L_{S1}^{o}\ (1 + 0.086\ f/T)$$

and

$$dL_{S1}/dT = -\ L_{S1}^{o} \times 0.086\ f/T^2 \qquad (10)$$

To obtain an accuracy in the temperature measurement of one millidegree at 5°K it was necessary to measure L_{S1} with a relative accuracy of $10 \times 10^{-6}\ f$ and $3.4 \times 10^{-6}\ f$ in the case of manganese ammonium tuttonsalt and potassium chromium alum respectively. The volume fraction of C_{S1} filled by the salt crystal ($2r$ = 19 mm) was 0.58 while experimentally f was found to be 0.28. With f = 0.28 it is necessary to measure the mutual inductance with a relative accuracy of about 10^{-6} to detect a temperature variation of one millidegree at 5°K with potassium chromium alum.

The number of turns of the Hartshorn bridge could be read with a precision of 0.001 turn. 1 turn corresponded to 3 μH, thus changes of the inductance could be measured to about 3×10^{-9}H. Actually L_{S1} was 14 mH, in this case a change of about 2×10^{-7} in L_{S1} could be measured.

The large value of the coefficient of mutual inductance made it necessary to use a rather large number of turns for the coils. A relatively low number of turns was chosen for the primary coil in order to avoid too large a heat input by the primary current. For the secondary coil rather thin wire was used (0.05 mm diameter) because of the limited space.

The measuring frequency was 227 Hz, the voltage change induced when the setting of the bridge was changed by 0.001 turn was 10^{-7} V at a measuring current of 25 mA. This could be detected easily at liquid helium and hydrogen temperatures.

3b. *Construction of the coils*

The primary coil of the set of mutual inductance coils in the dewar was wound with Povin insulated copper wire of 0.1 mm diameter.

The coil had two layers, each layer impregnated with cellulose lacquer. The field of this coil was made homogeneous by an extra coil on each end of the main coil. The resulting field is shown in fig. 3. The number of turns of the main coil was 2387 and the two extra coils had 209 turns in total. The

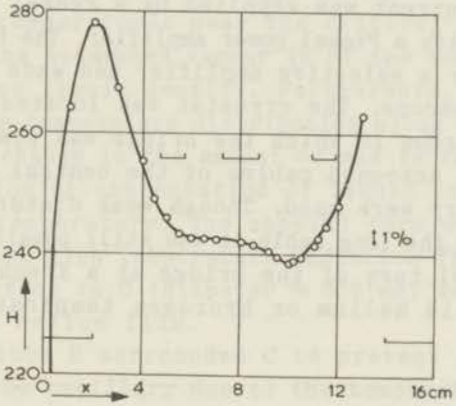

Fig. 3

The field of the primary coil as measured with a small coil. *H* is expressed in an arbitrary unit, *x* is the distance from the lower side of the coil. The positions of the three secondary coils and of the two extra primary coils are indicated.

resistance was 625 Ω at room temperature and 11 Ω at liquid helium and hydrogen temperatures. When a current of 25 mA flowed through the coil the field at the centre was about 5 Oe. The secondary coils were wound very carefully. Povin insulated copper wire of 0.05 mm diameter wound on a paper layer was used. Each layer was impregnated with dilute cellulose lacquer. The main coil C_{S1} consisted of 8 layers with 1728 turns in total. C_{S2} had 845 turns in 6 layers and C_{S3} 908 turns in 6 layers. The resistance of the three coils together was 2200 Ω at room temperature and 50 Ω at liquid helium and hydrogen temperatures. The three secondary coils were connected in such a way that the voltage induced in C_{S2} and C_{S3} opposed the voltage induced in C_{S1}.

3c. The bridge

The Hartshorn bridge has been discussed by Van der Marel, Van den Broek and Gorter [28] and also extensively by Van der Marel [29]. The current was supplied by a Peekel *RC* generator in combination with a Peekel power amplifier. The bridge signal was amplified by a selective amplifier and made visible on a Philips oscilloscope. The cryostat was located at about 36 meter from the room in which the bridge was placed. For the connection, the screened cables of the central cable system of the laboratory were used. Though weak disturbancies were introduced along the long cable it was still possible to detect changes of 0.001 turn of the bridge at a frequency of 227 Hz and at liquid helium or hydrogen temperatures.

3d. The crystals

The single crystal of manganese ammonium tuttonsalt which was difficult to prepare, was made in cooperation with the Crystallographic Laboratory of the Technical University at Delft*. Small crystals suspended from nylon threads were turned slowly around in a saturated solution of the salt. The solution was placed in a thermostat whose temperature decreased slowly at a rate of about 0.3 degree per 24 hour. This was accomplished in a simple way by turning the adjusting screw of a mercury contact thermometer using a clock motor with a retardation mechanism. Single crystals of the desired size were obtained but they were not clear and exhibited small cracks. The crystals of potassium chromium alum were prepared in a similar way by the Crystallographic Laboratory at Delft. Spheres were ground from the crystals with a diameter of 19 mm.

---

*) We wish to express our sincere thanks to Dr. W.F. de Jong, of the Crystallographic Laboratory of the Technical University at Delft.

4. The vapour pressure measurement

4a. General remarks

The vapour pressure thermometer consisted of the reservoir Th, the tube C connecting the reservoir to the manometers and the jacket J (fig.2).

C was made narrow firstly to decrease the heat input into Th by radiation and heat conduction and secondly to keep its volume small. If the volume of the tube C was made large, it would have been difficult to keep the liquid level in Th under control at temperatures near the critical point where the density of the saturated vapour is of the same order of magnitude as the liquid density. Furthermore, if C was wide a change of the temperature distribution along C would cause an appreciable change in the amount of gas in the tube and thus an evaporation or condensation of liquid in Th which would change the temperature. The special form of the capillary was to prevent high temperature radiation from entering Th. The constriction in C (diameter ≈ 0.2 mm) was to reduce the flow of the helium film.

The second tube E surrounded C to prevent condensation of the gas in the capillary due to the temperature gradient in the dewar above the λ-point (see Ch.VI). The tube E surrounded C over its whole length in the dewar. This was done to decrease the effect of temperature changes in the vapour in the dewar on the temperature in Th.

4b. The manometers

The pressures to be measured ranged from 170 cm to 0.1 mm Hg for the helium region and from 170 cm to 5 cm Hg in the hydrogen region. The desired accuracy was the equivalent of a few tenths of a millidegree. Though this does not require an extraordinarily high relative accuracy in the pressure measurements some special precautions were taken. Four types of mercury manometers were used.

1. For the region from 170 cm to 78 cm Hg a long mercury manometer was used with an inner diameter of 16 mm and with a scale on the glass wall. It was closed at one end. The glass scale was calibrated against an invar scale, a small correction of at most 0.1 mm over 60 cm length was found. A disadvantage of such a long manometer is that large temperature gradients may occur along the tubes when the manometer is used in a non-thermostated room.

2. For the region from 78 cm to 10 cm Hg an ordinary closed end mercury manometer with an inner diameter of 18 mm was used. It was read with a Precision Tool Company cathetometer. The cathetometer scale was calibrated against an invar scale, the corrections were negligible. Corrections for the capillary depression could be neglected for these wide tubes for pressures above 10 cm Hg.

3. For the region from 100 mm to 7 mm Hg a specially designed short manometer was used. It was only 15 cm high and was placed in a heavy walled copper box to obtain uniformity of temperature all over the manometer. The inner diameter of the tubes was 33 mm. The menisci were illuminated from behind with a beam of parallel light. A small invar scale was placed between the two tubes. The cathetometer was only used to measure the heights of the menisci on the small invar scale. The corrections for the capillary depression were negligible.

4. For the region from 7 mm to 0.1 mm Hg a MacLeod gauge was used with which the pressures could be increased by factors of 100, 200 and 400. The pressures could be read on a calibrated glass scale.

An oil differential manometer with three legs was used to compare the pressures over the bath, in the jacket and in the vapour pressure thermometer bulb.

4c. Thermomolecular pressure effect

At low pressures the pressure measured at the end of the tube C had to be corrected for the thermomolecular pressure effect to get the actual pressure in Th. The corrections were calculated form the equations of Keesom, Weber and Schmidt [30]. These equations are difficult to handle, but recently Roberts and Sydoriak [31] published numerical data based on them. The pressure correction was multiplied by dT/dp taken from the helium vapour pressure temperature scale T_{58} to obtain the influence of the correction on the measured vapour pressure temperature. The result for two tubes with inner diameters of 2.0 and 1.5 mm is shown in fig. 4.

The main part of the pressure difference occurs where the temperature changes from room temperature to about 50°K, therefore the correction for a tube of 2.0 mm inner diameter was used, this being the diameter of the upper part of the tube C. The correction is of very little importance above 1.4°K.

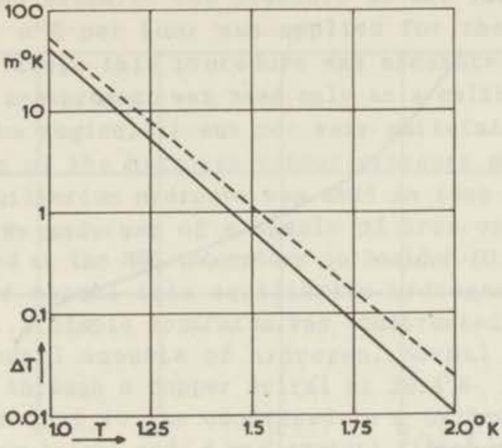

Fig. 4

The correction on the temperature measured with a vapour pressure thermometer filled with liquid helium due to the thermomolecular pressure difference. The solid and broken lines are for capillaries with inner diameters of 2.0 and 1.5 mm respectively.

4d. Aerostatic correction

A correction must be applied for the "aerostatic" pressure head of the gas column in the tube leading to the vapour pressure bulb. The exact calculation of this correction requires a knowledge of the temperature gradient along the tube. A correction was applied only for that part of tube C that was below the liquid surface of the bath assuming that the gas in this part of the tube has the density of the saturated vapour. The effect on the measured temperature is

$$\Delta T = \rho_G g h (\mathrm{d}T/\mathrm{d}p) \tag{11}$$

where ρ_G is the density of the saturated vapour, g the acceleration of gravity, h the length of the tube C below the liquid surface and $\mathrm{d}p/\mathrm{d}T$ the derivative of the pT relation of helium. In fig. 5 the length of the gas column h causing an error ΔT in the measured temperature of 1 m°K is given.

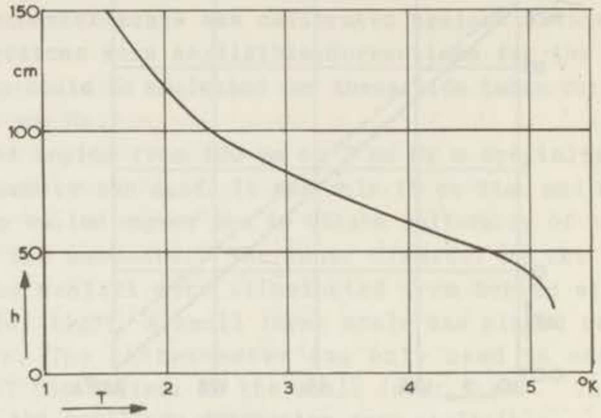

Fig. 5

The aerostatic head correction in a helium vapour pressure thermometer. h is the height of the column of helium vapour at saturated density that influences the measured temperature by 1 m°K.

It can be seen that the correction is usually small, becoming important only in the neighbourhood of the critical point. In the case of hydrogen the "aerostatic" head correction in our apparatus was negligible.

4e. The condensed gases

1. Helium. The helium gas was purified by passing it at high pressure over charcoal at liquid air temperature. As the amount of gas to be condensed was rather critical, the gas was admitted to a calibrated storage bulb of about 3.5 liter, and condensed from the bulb into the inner bath Th and into the jacket. Both were previously calibrated. The amount of liquid used was about 3.5 cm^3 in the inner bath and 1 cm^3 in the jacket.
2. Hydrogen. In the first experiments we used normal hydrogen from the laboratory stock without further purification. The normal hydrogen could be used only in the jacket. When it was condensed in the bulb Th the temperature rose far above the

bath temperature. Thus we filled the bulb with gas at one atmosphere and measured the pressure at the jacket. A correction of 1 m^{o}K per hour was applied for the ortho-para conversion. Though this procedure was accurate enough when the hydrogen measurement was used only as a calibration point for the helium region, it was not very satisfactory for the investigation of the hydrogen vapour pressure scale itself. Therefore equilibrium hydrogen was used in some of the later experiments. We made use of a sample of iron oxide, a catalyst developed at the NBS Laboratory in Boulder (U.S.A.) for the conversion of normal into equilibrium hydrogen in hydrogen liquefiers *. A simple apparatus was constructed for the conversion of small amounts of hydrogen. Normal hydrogen was first passed through a copper spiral at 20.4^{o}K for purification. After that it was condensed in a cylindrical copper vessel (of 9 cm height and 1.4 cm diameter) filled over a height of 5 cm with the catalyst. The liquid passed the catalyst at a rate of about 4 cm^{3} per hour. The composition of the converted hydrogen gas was determined by measuring the heat conductivity at 77^{o}K **. The average result was 98% para hydrogen.

5. Measurements with the empty coil

Several measurements were made without a paramagnetic salt to find the effect of the empty coil. At first sight the data were not very reproducible but then it appeared that the inductance was sensitive to pressure differences between the inner vessel and the dewar. When the pressure in the dewar remained constant and the pressure in the inner vessel was increased by one atmosphere the inductance increased by 0.034 turns of the bridge. This effect was reproducible. It was probably due to expansion of the glass tube on which the secondary coil was wound. In all further experiments the pressures at the outside and the inside of the secondary coils were kept equal.

Fig. 6a shows the results of measurements during January 1958. Between the first hydrogen measurement (Jan. 16) and the helium measurement the coils were kept at 77^{o}K, after the helium

---

* Our thanks are due to Dr. R.B.Scott of the Cryogenic Engineering Laboratory (NBS) for providing us with a sample of the catalyst.

** The analyses were made by Mr. H.J.M. van Beek and Mr. H.F.P. Knaap.

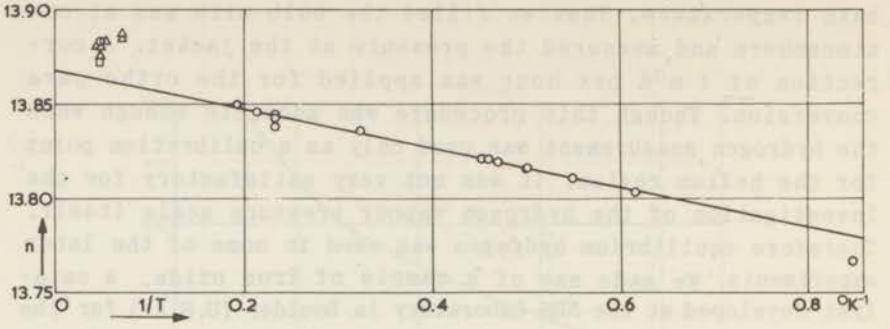

Fig. 6a

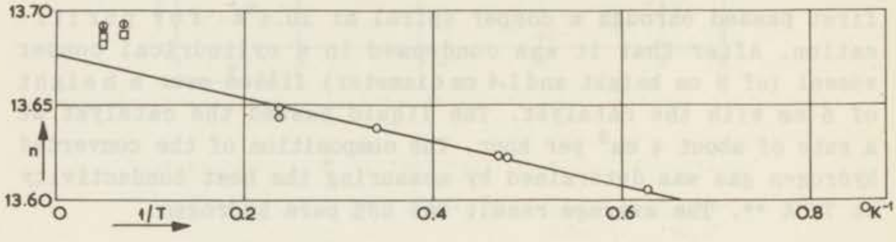

Fig. 6b

The mutual inductance of the empty coil measured in the number of turns of the Hartshorn bridge *n* at liquid helium and liquid hydrogen temperatures.

a. ⦶ H_2 Jan. 16   b. ⦶ H_2 Oct. 6
○ He Jan. 17   ○ He Oct. 7
□ H_2 Jan. 17   □ H_2 Oct. 7
△ H_2 Jan. 18

measurement the dewar was immediately filled with liquid hydrogen so that the temperature did not rise above 20.4°K. In the helium measurement as well as in the hydrogen measurements the sequence of the measured points was always from high to low and back to high temperatures in order to check the reproducibility. Fig. 6b shows the data of October 1958. The measurements were carried out in the way described above. Fig. 7 gives the data at hydrogen temperatures.
From figs. 6a and b and 7 it was concluded that the *n* versus *T* data for the empty coil could be represented by a straight line in the *n* versus *1/T* diagram with an additional correction in the hydrogen region as given in table I. The straight lines

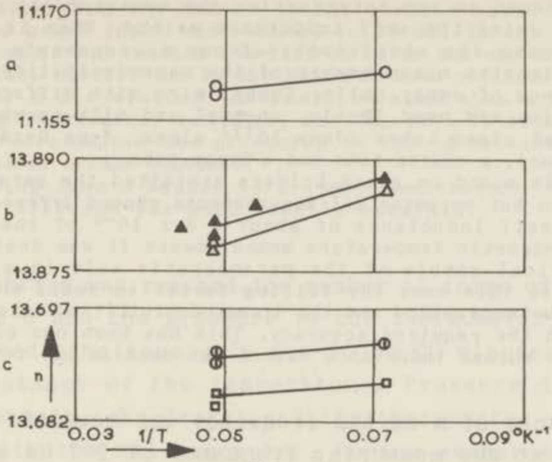

Fig. 7

The mutual inductance of the empty coil at hydrogen temperatures.

a. Sept. 18, 1957
b. Jan. 18, 1958 △ first series ▲ second series

c. ⦶ Oct. 6, 1958
□ Oct. 7, 1958

in figs. 6a and b represent a "negative paramagnetism" which is obviously due to the glass tubes. The upper and lower coils together contain more glass than the middle one. It was not necessary to introduce the correction represented by the straight lines in figs. 6a and b explicitly as it only changed the constant *B* in eq. (6); the correction was so small that its influence on Δ was negligible.

The inaccuracy in the correction at the boiling point of hydrogen was about ± 0.003 turn. This was also the order of the magnitude of the scattering of the points in the helium region. The mutual inductance of the middle secondary coil with respect to the primary was 14 mH, so that the relative uncertainty which corresponded to 9×10^{-9} H caused by the empty coil effect was about 0.6×10^{-6}.

TABLE I

Corrections for the empty coil in the hydrogen region.

T (°K)	Δn (turns)	T (°K)	Δn (turns)
23	- 0.017	14	- 0.021
20	- 0.018	11	- 0.024
17	- 0.019		

As mentioned in the introduction the measurements were started in 1949 using the self inductance method. When it was desired to increase the sensitivity of our measurements in 1955, we made extensive measurements of the reproducibility of the self inductance of empty coils. Copper wire with different types of insulation was used (Povin, enammel and silk-enammel) wound on different glass tubes (Jena 16^{III} glass, Jena Geräte glass and A.R. glass), a quartz tube and a brass tube.
The coils wound on glass holders exhibited the paramagnetism of the glass but moreover all measurements showed irreproducibilities in the self inductance of about $\pm 3 \times 10^{-6}$ of the inductance. In our magnetic temperature measurements it was desirable to use a spherical sample of the paramagnetic salt in a homogeneous field. In this case the filling factor is small when using the self inductance method and the irreproducibilities make it difficult to reach the required accuracy. This has been one of the reasons that the mutual inductance method was used in our further measurements.

The dependance of *n* on the frequency was measured and it was found that at the measuring frequency of 227 Hz a change of 1 Hz in the frequency changes *n* by 0.004 turns.

6. Procedure of measurements

The measurements with liquid helium proceeded as follows. When the helium had been siphoned into the dewar about 3 cm^3 of liquid was condensed in the thermometer vessel Th and about 1 cm^3 of liquid in the jacket. At any temperature to be measured the bath pressure was brought to the desired value.

The bath pressure was kept constant by manual control of the valves in the reducing line, or in the evaporating line when working above one atmosphere. Two oil differential manometers served as pressure indicators, one of the common type for pressures above one atmosphere and one with an inclined leg [32] to increase the sensitivity for pressures below one atmosphere. Below the λ-point a carbon thermometer in the bath served as the temperature indicator. Below 1.8°K the temperature was kept constant by varying the current through the heater again using the carbon thermometer as an indicator.

Keeping the bath temperature constant the pressure differences between the bath (measured at the cap of the cryostat just above the dewar), the jacket and the thermometer vessel were followed on the double oil differential manometer. After about 10-15 minutes temperature equilibrium was reached.

Above the λ-point the attainment of equilibrium required some precautions:
When going from a lower to a higher temperature the valve in the reducing or evaporating line was closed and the heater current switched on. A power of 100-500 mW was used depending on the amount of liquid in the bath. After some time small vapour bubbles appeared near the heater. At first they disappeared before reaching the surface but soon a constant flow

of bubbles from the heater to the surface could be observed. Then the power input was reduced to 35 mW. In the meantime the bath pressure had reached the desired value and was kept constant. Temperature equilibrium in the bath was then obtained immediately or after a few minutes (as could be seen when a metal vapour pressure thermometer was used, see Ch. VI). It took about 10-15 minutes more before the pressures in the jacket and the thermometer vessel became constant.
When going from a higher to a lower temperature the temperature equilibrium was more readily obtained.

When equilibrium was reached the number of turns of the Hartshorn bridge n and the pressure in the thermometer vessel p_{Th} were measured simultaneously for 10 to 20 minutes depending on the constancy of the temperature. Pressure differences between the bath, the jacket and the thermometer vessel were measured with the oil manometer. During measurements above the λ-point the power input of the heater was usually 35 mW. At temperatures near the critical point in most cases only a small amount of gas was in the jacket because much helium was necessary to fill it to saturation. In the first experiments the supporting metal strips described earlier were used at overpressures but later on a small table was simply placed under the surrounding nitrogen dewar. The cap of this dewar was fixed to the helium dewar. In this way the cryostat could stand pressures up to 180 cm Hg.

7. Experimental results with manganese ammonium tuttonsalt ($Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$)

7a. Presentation of the data

The measurements can be divided into four series. The data are listed in table II. In each of the series I, II, III and IV the salt was kept at liquid nitrogen temperature between measuring days. After each completed series the cryostat was warmed up to room temperature and the salt was removed. The positions of the crystal with respect to their crystalline axes were unknown. Before or after each helium day measurements at hydrogen temperatures were made to avoid errors due to changes of the inductance of the coils in time. For helium measurements the pressures given in table II are measured pressures in the thermometer vessel Th reduced to mm Hg at $0^{o}C$ and $g = 980.665\ \mathrm{cm/s^2}$. Corrections for the aerostatic head in the tube C and at the lowest temperatures also for the thermomolecular pressure effect expressed as temperature

TABLE II

Vapour pressures of liquid helium and hydrogen and corresponding bridge settings for manganese ammonium tuttonsalt.
ΔT for helium temperatures is the correction for the aerostatic pressure head or the thermomolecular pressure effect (*).
ΔT for hydrogen temperatures is the correction for the ortho - para conversion or for the hydrostatic pressure head (*).
Pressures are given in mm Hg at 0°C, ΔT in m°K.

p	n	ΔT
	Series IA	
May 14	Helium	
$p = p_{Th}$		
987.8	87.892	+ 0.9
773.10	92.823	+ 0.6
179.80	126.495	+ 0.3
36.614	170.627	+ 0.1
493.12	102.393	+ 0.2
984.4	87.963	+ 0.2
954.4	88.561	+ 0.2
939.0	88.889	+ 0.2
901.3	89.690	+ 0.1
870.4	90.397	+ 0.1
768.3	92.948	+ 0.1
982.1	87.996	+ 0.1
1466.7	80.495	+ 0.1
1315.2	82.463	+ 0.1
May 17	n-Hydrogen	
$p=p_{Jacket}$		
766.46	28.229	- 1
486.62	29.537	- 2
241.08	31.584	- 2
124.24	33.569	- 3
59.19	35.842	- 3
763.79	28.262	- 9
	Series IB	
May 24	Helium	
$p = p_{Th}$		
970.6	88.182	+ 1.2
846.3	90.896	+ 1.0
705.83	94.617	+ 0.8
210.22	122.385	+ 0.4
36.665	170.489	+ 0.2
12.41	202.788	+ 0.2
3.581	239.929	+ 0.1 - 0.7*
438.82	104.964	+ 0.1
771.54	92.823	

p	n	ΔT
May 28	n-Hydrogen	
$p=p_{Jacket}$		
777.48	28.178	- 2
116.56	33.721	- 3
89.79	34.514	- 4
222.95	31.778	- 5
441.14	29.793	- 6
772.32	28.204	- 8
771.61	28.202	- 1
	Series IC	
June 6	Helium	
$p = p_{Th}$		
43.07	164.987	+ 0.4
245.91	118.105	+ 0.5
768.4	92.570	+ 0.7
986.5	87.600	+ 0.7
1157.2	84.543	+ 0.8
1352.4	81.659	+ 0.8
1579.4	78.875	+ 0.9
1478.0	80.045	+ 0.5
1162.8	84.430	+ 0.4
956.3	88.183	+ 0.3
764.9	92.658	+ 0.2
237.65	118.952	+ 0.1
June 7	n-Hydrogen	
$p=p_{Jacket}$		
752.9	28.234	
267.48	31.192	
58.36	35.751	
245.87	31.451	
756.6	28.220	
	Series II	
Sept.25	n-Hydrogen	
$p=p_{Jacket}$		
773.0	27.972	- 6
295.67	30.746	- 7
60.89	35.512	- 8
767.35	27.996	- 9

TABLE III (continued)

p	n	ΔT
Sept.27	Helium	
$p = p_{Th}$		
997.5	88.597	+ 1.0
769.7	93.975	+ 0.9
501.16	103.491	+ 0.6
184.85	128.412	+ 0.4
41.895	172.165	+ 0.3
36.02	177.000	+ 0.2
	Series III	
Oct. 11	Helium	
$p = p_{Th}$		
34.32	170.662	
18.88	187.726	
8.208	211.930	
20.329	185.613	
35.63	169.529	
40.49	165.902	
93.21	142.546	
180.14	125.335	
320.71	111.342	
482.76	102.068	
768.44	92.258	
907.4	88.936	
1044.6	86.201	
1226.3	83.159	
Oct.15	n-Hydrogen	
$p=p_{Jacket}$		
767.51	28.063	- 9
	Series IVA	
Nov.28	Helium	
$p = p_{Th}$		
776.13	93.027	+ 1.0
242.47	119.964	+ 0.5
41.899	169.405	+ 0.1
238.47	120.392	+ 0.4
771.82	93.160	+ 0.5
1093.3	86.129	+ 0.5
1546.8	79.604	+ 0.5
1091.4	86.117	+ 0.2
763.65	93.078	+ 0.1
Nov.29	n-Hydrogen	
$p=p_{Bath}$		
773.50	27.925	+ 13* - 26
773.51	27.932	+ 13* - 28
Nov. 30	n-Hydrogen	
$p=p_{Jacket}$		
780.19	27.931	- 48
	Series IVB	
Dec. 13	Helium	
$p = p_{Th}$		
778.76	95.824	+ 1.0
876.1	93.377	+ 1.0
967.35	91.366	+ 1.1
1254.2	86.303	+ 1.2
1517.2	82.783	+ 1.5
1640.8	81.385	+ 1.6
1626.8	81.556	
Dec. 14	n-Hydrogen	
$p=p_{Jacket}$		
753.10	30.804	
Dec. 18	e-Hydrogen	
$p = p_{Th}$		
799.52	30.728	+ 2
609.52	31.500	+ 2
438.69	32.463	+ 2
301.72	33.558	+ 2
202.90	34.756	+ 2
130.32	36.095	+ 2
85.80	37.377	+ 2
85.07	37.396	+ 2
59.90	38.514	+ 2
59.60	38.520	+ 2
84.31	37.420	+ 2
133.50	36.008	+ 2
132.85	36.021	+ 2
206.43	34.700	+ 2
292.58	33.657	+ 2
290.95	33.671	+ 2
440.26	32.450	+ 2
784.93	30.784	+ 2
786.26	30.781	+ 2
783.89	30.788	+ 2
1052.0	29.952	+ 2
1346.2	29.276	+ 2
1530.5	28.241	+ 2
1051.2	29.966	+ 2
783.26	30.782	+ 2

corrections are given in the table. They were calculated in the way described in section 4. For the data of Oct. 11 no aerostatic head correction was applied as this correction did not exceed one tenth of a millidegree. The number of turns at hydrogen temperatures given in table II has been corrected according to table I. In the measurements with normal hydrogen the gas was condensed in the jacket only and the pressures given in table II are pressures measured in the jacket. The temperature correction ΔT is for the ortho-para conversion. It was calculated on the basis of "1 m^oK per hour".

On Nov. 29 the pressure was measured at the bath and a correction for the hydrostatic pressure head was applied. On Dec. 18 equilibrium hydrogen was used and condensed in the inner vessel Th and in the jacket. The pressures in the table are those of the inner vessel. The estimated concentration was 2 percent ortho hydrogen. Therefore when the scale for equilibrium hydrogen is used to convert the pressures into temperatures, a correction of + 2 m^oK has to be applied to the temperature.

7b. *Comparison with* T_{L55} *and* T_{55E}

As an illustration of the general behaviour of the data $n - 344.7/T$ is plotted versus $1/T$ in fig. 8 for series IA. The temperatures were obtained from the vapour pressures and corrections given in table II using T_{L55} in the helium region and T_V for normal hydrogen in the hydrogen region* . $n - 344.7/T$ was plotted instead of n versus $1/T$ in order to make the small deviations from a straight line visible. It was found to be possible to represent the data within the limits of accuracy of the T_V and T_{L55} scales by an equation $n = A + B/(T + \Delta)$ in the helium as well as in the hydrogen region. The curve drawn in fig. 8 represents $n = A + B/(T + \Delta)$ in which A, B and Δ are determined in such a way that the curve fits the data at 4.22 and 2.2°K and at the boiling point of hydrogen lies the equivalent of 18 m^oK below the average of the points. The deviations of the data from the curve can now be interpreted as errors in the T_V and T_{L55} scales. Of course the errors found depend on the choice of the curve. For the hydrogen scale the choice was such that the deviation from the

---

*) The T_V scales for normal and equilibrium hydrogen are defined by eqs.(4) and (5) in Chapter V.

T_V scale at 20.4°K was 18 m°K (this brings the boiling point of normal hydrogen to 20.378°K, see Ch. V), the deviation at 14°K became about 20 m°K in the same direction. Assuming that T_{L55} was correct at 4.22 and 2.2°K there was a pronounced deviation above 4.2°K. By comparison of fig. 8 with fig. 6 it can be seen that the uncertainties in the empty coil corrections were negligible. Even the whole correction in the hydrogen region had only a very minor influence on the behaviour of the curve in the helium region.

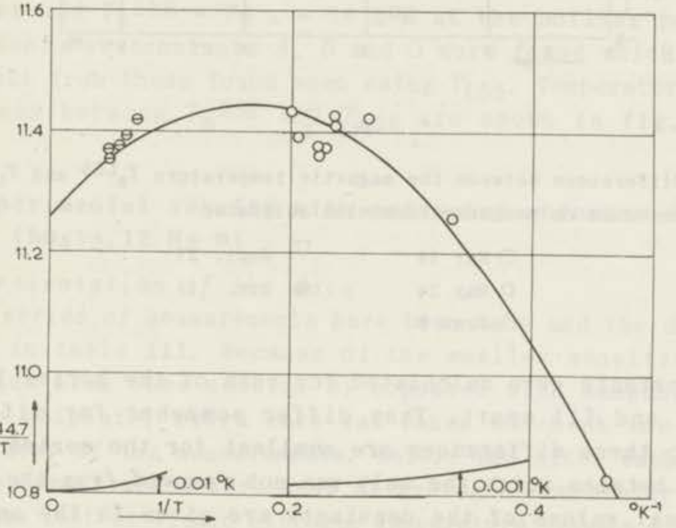

Fig. 8

Data from series IA (table II) compared with the T_{L55} scale for helium and the T_V scale for normal hydrogen.

For a more precise comparison with T_{L55} the following procedure was followed. Temperatures were calculated from the pressures and corrections in table II using T_{L55} and T_V. A temperature T_m^{L55} was defined by the equation

$$n = A + B/(T_m^{L55} + \Delta) \qquad (12)$$

in which the constants A, B and Δ were determined in such a way that $T_m^{L55} = T_{L55}$ at the boiling point of helium and near the λ-point and $T_m^{L55} - T_V = -18$ m°K at the boiling point of normal hydrogen.

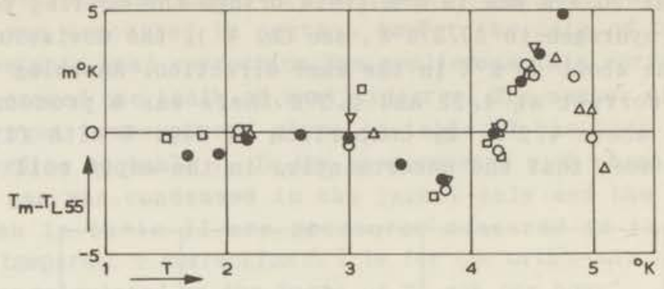

Fig. 9

Differences between the magnetic temperature T_m^{L55} and T_{L55} for data on manganese ammonium sulphate.

○ May 14
□ May 24
△ June 6
▽ Sept. 27
● Oct. 11

The constants were calculated for each of the series IA, IB, IC, II and III apart. They differ somewhat for different series; these differences are smallest for the series IA, IB and IC between which the salt was not removed from the dewar. Numerical values of the constants are given in the analysis using T_{58} (see Ch. IV). The differences between T_m^{L55} and T_{L55} are shown in fig. 9.

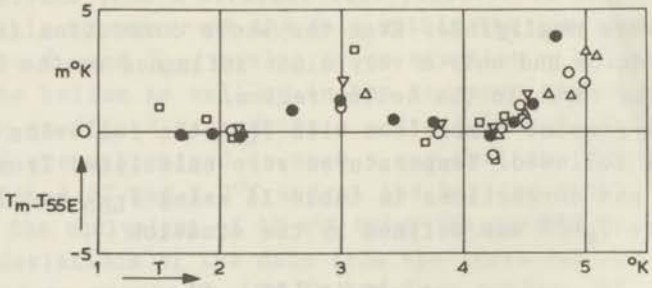

Fig. 10

Differences between the magnetic temperature T_m^{55E} and T_{55E} for data on manganese ammonium sulphate.
Measurements on different days are indicated as in fig. 9.

In just the same way the results were compared with T_{55E} by defining a temperature $T_m{}^{55E}$ with the equation

$$n = A + B/(T_m{}^{55E} + \Delta) \qquad (13)$$

in which the constants were determined from the condition $T_m{}^{55E} = T_{55E}$ at the boiling point of helium and near the λ-point and $T_m{}^{55E} - T_V = -18$ m°K at the boiling point of hydrogen. New constants A, B and Δ were found which differ somewhat from those found when using T_{L55}. Temperature differences between $T_m{}^{55E}$ and T_{55E} are shown in fig. 10.

8. Experimental results with potassium chromium alum ($K\ Cr\ (SO_4)_2 . 12\ H_2\ O$)

8a. Presentation of the data

Three series of measurements have been made and the data are given in table III. Because of the smaller sensitivity of chromium alum (see section 3) compared with manganese ammonium sulphate, extra care was taken to check the reproducibility of the measurements. Before and after each helium series measurements were made at hydrogen temperatures. The salt was kept at liquid nitrogen temperature between the first hydrogen measurements and the helium measurements of each series IA, IB and II and after the helium measurements the hydrogen was immediately transferred into the dewar so that the temperature of the salt did not rise above 20.4°K. Part of the hydrogen measurements were carried out with normal and part with equilibrium hydrogen. For all measurements with e-H_2 a correction of 2 m°K was used for the incomplete conversion.

The measurements of series III were carried out in a somewhat different way. The plug P (see fig. 2) was replaced by a similar plug with several holes so that the inner vessel was in direct contact with the outer bath. The purpose was to measure at temperatures below 1.5°K by measuring the pressure at the bath to omit corrections for the thermomolecular pressure effect and a possible film effect. However we did not succeed in making reliable pressure measurements below 1.2°K and the points below 1.4°K must be omitted due to uncertainties in the MacLeod calibration. The other points are in agreement with the series measured with the closed plug.

T A B L E III

Vapour pressures of liquid helium and hydrogen and corresponding bridge settings for potassium chromium alum. The temperature corrections ΔT are the same as indicated in table II except for March 28 where ΔT means the hydrostatic head correction. Pressures are given in mm Hg at $0^{o}C$, ΔT in $m^{o}K$.

p	n	ΔT
	Series IA	
Feb. 6	e-Hydrogen	
$p = p_{Th}$		
781.20	16.837	+ 2
779.40	16.843	+ 2
Feb. 7	Helium	
$p = p_{Th}$		
1369.6	34.800	+ 1.3
1034.7	36.567	+ 0.7
754.58	38.680	+ 0.5
342.17	44.501	+ 0.3
135.93	52.172	+ 0.2
40.63	63.388	+ 0.1
132.92	52.371	+ 0.1
352.03	44.289	+ 0.1
752.47	38.702	+ 0.1
343.25	44.472	+ 0.3
512.62	41.436	+ 0.3
756.86	38.661	+ 0.3
1017.9	36.675	+ 0.2
1170.1	35.778	+ 0.1
Feb. 8	n-Hydrogen	
$p = p_{Bath}$		
753.70	16.832	+ 15* - 13
Feb. 9	n-Hydrogen	
$p = p_{Bath}$		
748.92	16.842	+ 8* - 25
	Series IB	
Feb. 17	n-Hydrogen	
$p = p_{Bath}$		
764.26	16.813	+ 9* - 4

p	n	ΔT
Feb. 18	Helium	
$p = p_{Th}$		
1481.6	34.327	+ 1.5
1277.5	35.226	+ 0.9
991.8	36.833	+ 0.6
769.24	38.539	+ 0.5
550.45	40.903	+ 0.3
397.40	43.341	+ 0.2
239.19	47.370	+ 0.2
231.05	47.648	+ 0.5
135.09	52.228	+ 0.4
78.512	57.131	+ 0.3
36.956	64.328	+ 0.2
17.207	71.700	+ 0.2
5.841	82.448	+ 0.1 - 0.3*
3.484	87.686	+ 0.1 - 0.7*
5.882	82.337	+ 0.1 - 0.3*
37.359	64.238	+ 0.1
78.528	57.112	+ 0.1
144.11	51.668	+ 0.1
762.14	38.611	
Feb. 19	n-Hydrogen	
$p = p_{Bath}$		
765.50	16.811	+ 10* - 14
Feb. 21	e-Hydrogen	
$p = p_{Th}$		
779.31	16.837	+ 2

TABLE III (continued)

p	n	ΔT
Series IIA		
March 12	n-Hydrogen	
$p = p_{Bath}$		
760.8	16.774	+ 7* - 4
March 13	Helium	
$p = p_{Th}$		
1591.6	33.778	+ 1.7
1428.1	34.416	+ 1.0
1124.8	35.893	+ 0.6
922.9	37.171	+ 0.5
761.58	38.465	+ 0.4
612.97	39.983	+ 0.3
451.42	42.212	+ 0.2
453.20	42.184	+ 0.9
302.62	45.295	+ 0.7
185.58	49.297	+ 0.5
115.61	53.394	+ 0.5
69.512	58.036	+ 0.4
35.221	64.542	+ 0.3
24.826	67.898	+ 0.3
41.167	63.021	+ 0.3
68.945	58.121	+ 0.3
114.32	53.510	+ 0.3
182.45	49.455	+ 0.3
299.91	45.381	+ 0.3
449.62	42.264	+ 0.3
613.61	39.995	+ 0.3
759.01	38.511	+ 0.3
916.8	37.234	+ 0.3
1123.0	35.918	+ 0.2
1430.2	34.418	+ 0.1
1595.1	33.771	+ 0.1
March 14	n-Hydrogen	
$p = p_{Bath}$		
762.0	16.774	+ 14* - 12
Series IIB		
March 19	n-Hydrogen	
$p = p_{Bath}$		
765.25	16.769	+10* - 5

p	n	ΔT
March 20	Helium	
$p = p_{Th}$		
778.75	38.340	+ 1.1
1455.35	34.314	+ 1.5
1677.9	33.482	+ 1.0
March 21	e-Hydrogen	
$p = p_{Th}$		
798.79	16.764	+ 2
796.93	16.759	+ 2
Series III		
March 27	n-Hydrogen	
$p = p_{Bath}$		
750.64	16.592	+ 5* - 5
March 28	Helium	
$p = p_{Bath}$		
762.95	37.772	+ 7.0
36.861	62.923	
25.623	66.349	
6.691	79.180	
6.261	79.850	
14.200	71.925	
24.816	66.669	
32.208	64.214	
36.837	62.941	
241.84	46.243	+ 3.6
522.86	40.436	+ 1.6
750.63	37.927	
March 29	drogen	
$p = p_{Bath}$		
756.86	16.593	+ 15* - 23

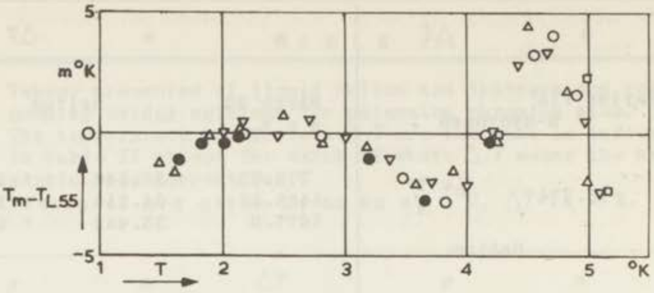

Fig. 11

Differences between the magnetic temperature T_m^{L55} and T_{L55} for data on potassium chromium alum.

○ Feb . 7
△ Feb . 18
▽ March 13
□ March 20
● March 28

8b. *Comparison with T_{L55} and T_{55E}*

The data were compared with T_{L55} and T_{55E} in the way described for manganese ammonium sulphate. The results are shown in figs. 11 and 12. Numerical values of the constants *A* and *B* will be given in the analysis using T_{58} (see Ch. IV).

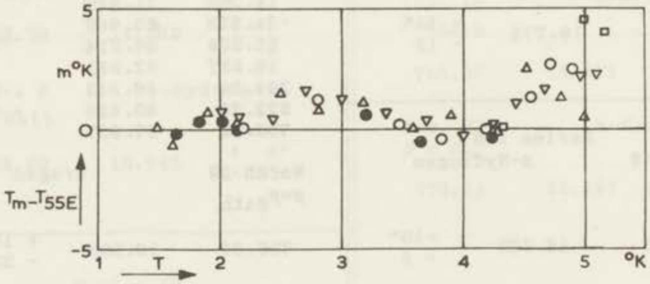

Fig. 12

Differences between the magnetic temperature T_m^{55E} and T_{55E} for data on potassium chromium alum. Measurements on different days are indicated as in fig. 11.

9. Pressure differences between the thermometer vessel, the jacket and the bath

As mentioned, during all measurements pressure differences between the pressures over the bath, in the thermometer vessel Th and in the jacket J were measured. The pressure differences were corrected for the aerostatic head in the tubes C and E. Temperature differences were derived using d*p*/d*T* from the *pT* relation for helium or hydrogen.

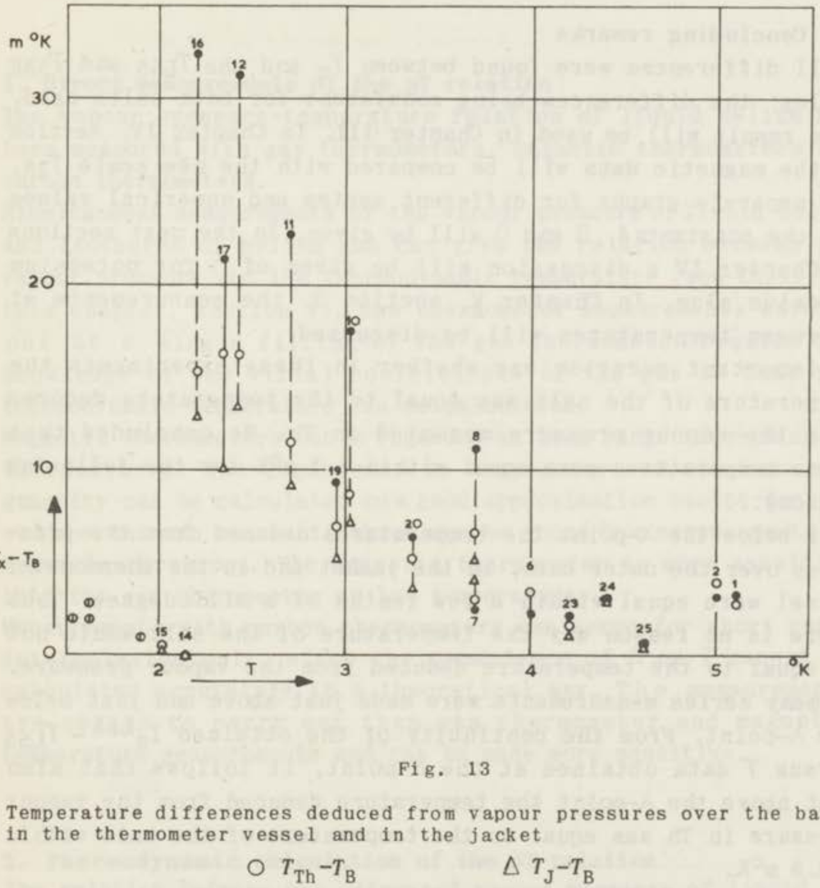

Fig. 13

Temperature differences deduced from vapour pressures over the bath, in the thermometer vessel and in the jacket

○ $T_{\mathrm{Th}}-T_{\mathrm{B}}$ △ $T_{\mathrm{J}}-T_{\mathrm{B}}$

The black points indicate the calculated hydrostatic head correction at the height of Th.

Fig. 13 is a typical plot of results obtained in the case of helium. At higher temperatures where the hydrostatic head corrections were small the temperature in Th was approximately equal to the temperature deduced from the pressure over the bath increased by the hydrostatic head in the liquid. At lower temperatures (above the λ-point) especially when the liquid level was high, the temperature was appreciably lower than calculated from the bath pressure and the hydrostatic head. The jacket temperature was generally somewhat lower than the temperature of Th. Just below the λ-point the bath, thermometer and jacket temperatures were equal. A further discussion will be given in Chapter VI.

10. Concluding remarks

Small differences were found between T_m and the T_{L55} and T_{55E} scales; the differences being consistent for both salts used. This result will be used in Chapter III. In Chapter IV, section 1, the magnetic data will be compared with the new scale T_{58}, and separate graphs for different series and numerical values for the constants A, B and Δ will be given. In the next sections of Chapter IV a discussion will be given of Δ for potassium chromium alum. In Chapter V, section 2, the measurements at hydrogen temperatures will be discussed.

An important question was whether in these experiments the temperature of the salt was equal to the temperature deduced from the vapour pressure measured in Th. We concluded that these temperatures were equal within ± 1 m°K for the following reasons:

Just below the λ-point the temperatures deduced from the pressures over the outer bath, in the jacket and in the thermometer vessel were equal within a few tenths of a millidegree. Thus there is no reason why the temperature of the salt would not be equal to the temperature deduced from the vapour pressure. In many series measurements were made just above and just below the λ-point. From the continuity of the obtained $T_m^{L55} - T_{L55}$ versus T data obtained at the λ-point, it follows that also just above the λ-point the temperature deduced from the vapour pressure in Th was equal to the temperature of the salt within ± 0.5 m°K.

A second justification is that the data did not depend on the level of the liquid in the dewar, on the heating current, or on the amount of helium condensed in Th.

CHAPTER III

THE VAPOUR PRESSURE-TEMPERATURE RELATION OF LIQUID ^{4}He

1. Direct measurements of the pT relation

The vapour pressure-temperature relation of liquid helium has been measured with gas thermometers, magnetic thermometers and carbon thermometers.

Simultaneous measurements of the vapour pressure of liquid helium and isotherms of helium gas can give the relation between the vapour pressure and the thermodynamic temperature (see Ch.I. and this chapter, section 7). Gas thermometer measurements carried out at a single filling of the gas thermometer require the knowledge of the virial coefficients of the gas so that the thermodynamic temperature can be calculated.

Magnetic thermometers can be regarded as long range interpolation thermometers. The dependence on temperature of the measured quantity can be calculated to a good approximation except for two or three unknown constants which must be found from measurements at known temperatures. The magnetic thermometer is more sensitive than the gas thermometer at low temperatures.

Measurements with carbon thermometers can serve for short range interpolation only, since the dependence of R on T cannot be calculated accurately in a theoretical way. The measurements are easier to carry out than gas thermometer and magnetic temperature measurements and can be made more sensitive.

2. Thermodynamic calculation of the pT relation

The relation between the saturated vapour pressure of liquid helium and the thermodynamic temperature can be determined not only from direct vapour pressure measurements, but also by thermodynamic calculations based on thermal and *pVT* data of the liquid and gaseous states. A short description of the thermodynamic equations involved will be given.

The saturated vapour pressure of liquid helium can be written as

$$\ln p = i - \frac{L_0}{RT} + \frac{5}{2} \ln T - \frac{1}{RT} \int_0^T S_L \, dT + \frac{1}{RT} \int_0^p V_L \, dp + \epsilon \qquad (1)$$

$$\epsilon = \ln \frac{pV_G}{RT} - \frac{2B}{V_G} - \frac{3C}{2V_G^2} \qquad (2)$$

$i = \ln (2\pi m)^{3/2} k^{5/2} h^{-3}$

m is the mass of a ^{4}He atom, k is Boltzmann's constant and h Planck's constant

R is the gas constant

L_0 is the latent heat of vaporization per mole at $T = 0^\circ$K

S_L is the molar entropy of the liquid

V_L is the molar volume of the liquid

V_G is the molar volume of the gas

B and C are the virial coefficients of the gas defined by the equation of state

$$p\,V_G = RT\left(1 + \frac{B}{V_G} + \frac{C}{V_G^2}\right) \qquad (3)$$

Eq. (1) can be derived starting from the equality of the Gibbs free energies of the liquid and gaseous states [8,3]. It is assumed in the calculation of ϵ that the influence of higher virial coefficients can be neglected.

The chemical constant i and R are known accurately. At present L_0 cannot be calculated accurately from first principles. The entropy integral can be calculated from the measured specific heat of the liquid along the saturation line C_L using the equation

$$S_L = \int_0^T (C_L/T)\,dT \qquad (4)$$

A difficulty in this calculation is that the older specific heat data were measured using old temperature scales. For the recalculation of these data to a new scale it is often necessary to go back to the calibration of the secondary thermometers used. $\int_0^p V_L \, dp$ can be evaluated from experimental data on the liquid density. The term ϵ represents the influence of the non-ideality of the gas. It can be calculated using experimental B and C values.

It follows that except for the so far unknown constant L_0, p can be calculated when C_L, V_L and the virial coefficients are known.

The accuracy obtained depends, of course, on the accuracy of the experimental data. The term $\int_0^p V_L \mathrm{d}p$ is only of minor importance. L_0 can be determined by fitting eq. (1) to the data of vapour pressures and corresponding temperatures obtained with gas thermometers.
Another approach is to use Clapeyron's equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T\,(V_G - V_L)} \tag{5}$$

in which L is the heat of vaporization per mole. In recent experiments not L itself but the so called apparent heat of vaporization L_a has been measured. L_a is defined as the amount of heat necessary to liberate one mole of helium gas from a calorimeter containing liquid helium.

$$L = L_a\,(1 - V_L/V_G) \tag{6}$$

L_a is larger than L because when one mole of liquid is evaporated a fraction of the gas produced occupies the space of the evaporated liquid. It follows from eqs. (5) and (6) that

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L_a}{T\,V_G} \tag{7}$$

which taking eq. (3) into account can be written as

$$-\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)} = \frac{L_a}{R(1 + B/V_G + C/V_G^2)} \tag{8}$$

The calculation of d ln p / d $(1/T)$ from eq. (8) depends only on L_a and the virial coefficients. At higher temperatures the influence of the virial coefficients is appreciable ($B/V_G + C/V_G^2 \approx 0.33$ at 4.2°K) but below about 2.7°K it is small ($B/V_G + C/V_G^2 < 0.1$) and equation (8) is very simple.
The pT relation can be calculated when C_L, V_L and the virial coefficients are known in the whole temperature region and L_a is known at one pressure. L_0 can then be determined from eqs. (1) and (8). When L_a is known over the whole temperature range, the internal consistency of the C_L, V_L, B, C and L_a data can be checked.
A direct determination of L_0 from eqs. (1) and (8) without significant interference of the correction terms would be possible if L_a was known at low enough temperatures (e.g. below about

$1.6^{\circ}K$). Instead of eq. (5) the following equation may also be used

$$L = L_o + \frac{5}{2} RT - \int_o^T C_L \, dT - \int_o^p V_L \, dp + \frac{RT}{V_G} (B - T \frac{dB}{dT}) + \frac{RT}{V_G^2} (C - \tfrac{1}{2} T \frac{dC}{dT}) \tag{9}$$

Eq. (9) can be derived from (1) and (5) [8].

A complication in the thermodynamic calculation of the pT relation in the case of ^{4}He is the second order transition at the λ-point with the corresponding peak in the specific heat curve. This also causes a dip in the L versus T curve at the λ-point. This makes it impossible to represent the pT relation by a simple analytical function in the whole temperature region.

During the last years when the helium temperature scale has been in discussion several authors who published data on C_L, V_L, B, C and L_a calculated the influence of their measured values on the pT relation.

3. Temperature scales up to 1955

3a. *The development before 1955*

The first complete helium temperature scale was the 1924 scale. At that time the λ-phenomenon was not yet sufficiently understood and the vapour pressure was given as a simple analytical function of the temperature over the temperature range between 5.2 and $1.475^{\circ}K$. Below $1.475^{\circ}K$ the thermodynamically calculated pT relation of Verschaffelt was used. The 1924 scale was succeeded by the 1929 scale, the 1932 scale, the 1937 scale, the 1939 scale and the 1948 scale. These scales are extensively discussed in ref. 27. They were based for the greater part on gas thermometer measurements made at Leiden; the 1937, 1939 and 1948 scales below $1.5^{\circ}K$ were based on thermodynamic calculations and magnetic temperature measurements made in Oxford and Leiden. The differences between these scales and T_{58} [9] are shown in fig. 14. Numerical values are given in ref. 33.

When the 1948 scale was adopted by a Commission of the I.U.P.A.P. in Amsterdam [6,33] errors in the scale had already been found by Kistemaker from isotherm and gas thermometer measurements and they had been checked to some extent by a thermodynamic calcu-

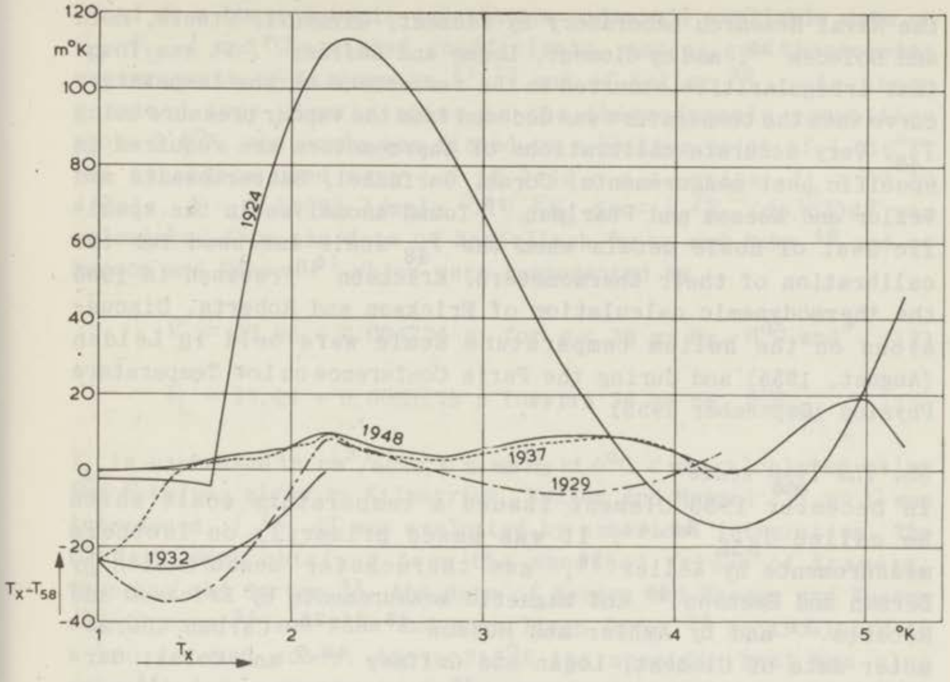

Fig. 14

Temperature differences T_X-T_{58} where X denotes different scales as indicated in the figure.

lation [22,23]. These errors in T_{48} were confirmed by the magnetic measurements of Van Dijk e.a. [18] and were found consistent with measurements on the helium three vapour pressure by Abraham, Osborne and Weinstock [34]. In 1953 Erickson and Roberts published the results of magnetic measurements on iron ammonium alum and manganese ammonium sulphate and made an improved thermodynamic calculation [21].

Berman and Swenson made gas thermometer measurements between 4.2 and 5.2°K [35]. Isotherm measurements combined with vapour pressure measurements between 1.5 and 4.0°K using ^{4}He gas and ^{3}He gas were performed by Keller [36].

Further results of magnetic temperature measurements were obtained by Van Dijk and Durieux in 1954 [18]. Magnetic thermometer measurements were also made by Ambler and Hudson [24,25]. Measurements with carbon thermometers between 4.2 and 5.2°K were made by Worley, Zemansky and Boorse [37].

An extensive investigation with carbon thermometers was made at the Naval Research Laboratory by Clement, Quinnell, Steele, Hein and Dolecek [38], and by Clement, Logan and Gaffney [7]. It was found that irregularities occurred in the resistance versus temperature curve when the temperature was deduced from the vapour pressure using T_{48}. Very accurate calibrations of thermometers are required in specific heat measurements. Corak, Garfunkel, Satterthwaite and Wexler and Keesom and Pearlman [39] found anomalies in the specific heat of noble metals when the T_{48} scale was used for the calibration of their thermometers. Erickson [40] revised in 1955 the thermodynamic calculation of Erickson and Roberts. Discussions on the helium temperature scale were held in Leiden (August, 1955) and during the Paris Conference on Low Temperature Physics (September 1955) [41,42].

3b. The T_{55E} scale

In December 1955 Clement issued a temperature scale which he called $T_{55\mathrm{E}}$ [43,44]. It was based primarily on isotherm measurements by Keller [36], gas thermometer measurements by Berman and Swenson [35] and magnetic measurements by Erickson and Roberts [21] and by Ambler and Hudson [45,24,25]. Carbon thermometer data of Clement, Logan and Gaffney [46,7] and Corak, Garfunkel, Satterthwaite and Wexler [39] and of Clement e.a. [38] were used by making the scale such that $\Delta \log R/\Delta(1/T)$ versus T was a smooth curve which could be extrapolated in a reasonable way to hydrogen temperatures. Furthermore it was tried to make the first derivative dp/dT of the scale agree with the heat of vaporization data of Dana and Kamerlingh Onnes [47] and of Berman and Poulter [48]. The $T_{55\mathrm{E}}$ scale was defined by the equations:

$$\ln p(\mathrm{mm\ Hg}, 0^{\circ}\mathrm{C}) = 6.22077 - \frac{8.3861}{T} + 0.945 \ln T + 0.2475\, T \quad \text{for } T > 2.1735^{\circ}\mathrm{K} \qquad (10)$$

and

$$\ln p(\mathrm{mm\ Hg}, 0\ \mathrm{C}) = 5.04862 - \frac{7.18132}{T} + 2.5 \ln T - 4.75 \times 10^{-5} T^{9} \quad \text{for } T < 2.1735^{\circ}\mathrm{K} \qquad (11)$$

p is expressed in mm Hg at 0°C and standard gravity ($g = 980.665$ cm/s^2). At $T = 2.1735^{\circ}$K p and dp/dT are continuous but d^2p/dT^2 is discontinuous. The pressure at $T = 2.1735^{\circ}$K is 37.864 mm Hg at 0°C.

3c. The T_{L55} scale

In April 1956 Van Dijk and Durieux issued a temperature scale called $T_{\mathrm{L}55}$ (Leiden 1955) [49,8,27]. Up to 4.2°K this scale was based on a thermodynamic calculation using all available data on C_L, V_L, L and the virial coefficients, and on gas thermometer measurements of Kistemaker [22,23] and of Keller [36]. As there remained some uncertainties in the thermodynamic quantities above 3.0°K, the scale was fitted to a boiling point of 4.216°K. The constants used were $i = 12.2440$ c.g.s. units, $L_o = 59.50$ J/mole, $R = 8.31662$ J/mole °K. $\int_o^p V_L \, dp = \int_o^T V_L \, (dp/dT) dT$ was calculated from the data of Kamerlingh Onnes and Boks [50] and of Keesom and Keesom [51] which were represented by

$$V_L = 27.66 - 0.004734\ p \quad \text{for } p < 38 \text{ mm Hg, } 0^{o}\text{C and} \qquad (12)$$

$$V_L = 27.24 + 0.0063375\ p \quad \text{for } p > 38 \text{ mm Hg, } 0^{o}\text{C} \qquad (13)$$

V_L is expressed in cm^3/mole, p in mm Hg at 0°C. ϵ was calculated using the B values given by Kilpatrick, Keller and Hammel [52], no C was introduced. $\int_o^T S_L \, dT$ was evaluated by numerical integration. The C_L data were obtained from the smoothed values of Kramers, Wasscher and Gorter [53], the data of Keesom and Keesom and Keesom and Clusius [54] and Dana and Kamerlingh Onnes [55] recalculated to a provisional scale. Above 2.5°K the specific heat was also calculated from the heat of vaporization data of Dana and Kamerlingh Onnes [47] and of Berman and Poulter [48]. The final choice of C_L, which was in good agreement with the average of all data, was made in such a way that for $T = 4.216$°K $p = 760$ mm Hg at 0°C.

L_o was determined by fitting eq. (1) to the results of the gas thermometer measurements of Kistemaker and Keller from 1.5 up to 2.5°K because here the last three terms is eq. (1) are small. This result was in reasonable agreement with L_o calculated from the heat of vaporization data between 1.5 and 2.5°K [8].

The influences of the last three terms in eq. (1) are indicated in fig. 15, where ΔT_a, ΔT_b and ΔT_ϵ denote the change in the calculated scale arising from a one percent change of the terms $(1/RT) \int_o^T S_L \, dT$, $(1/RT) \int_o^p V_L dp$ and ϵ respectively.

The thermodynamic calculation could not be extended to above 4.2°K because no sufficiently accurate data were available. Therefore the scale was based from 4.2 to 5.2°K on Berman and Swenson's gas thermometer data [35] using the equation

$$\log p \text{ (mm Hg, } 0^{o}\text{C)} = 1.977254 - \frac{2.77708}{T} + \frac{5}{2} \log T \qquad (14)$$

Eq. (14) joined smoothly into the calculated scale below 4.2°K.

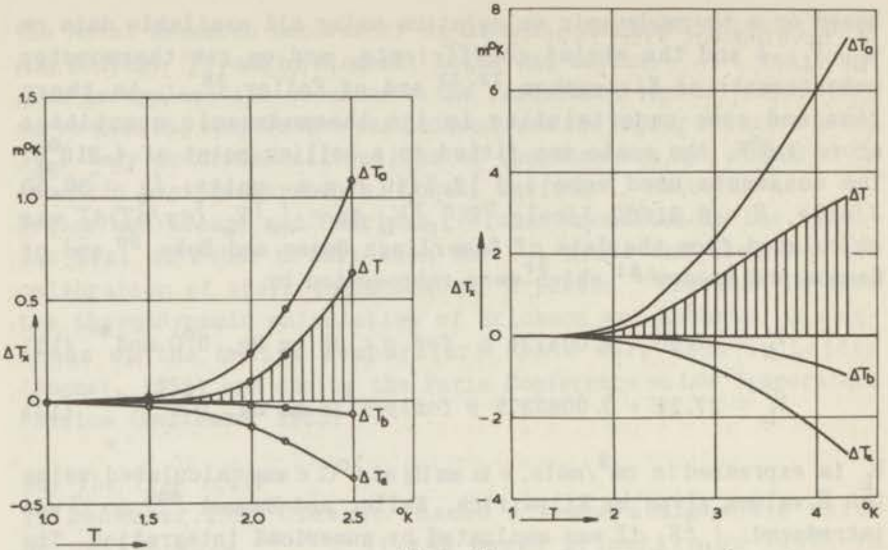

Fig. 15
The influence of different terms in eq. (1) on the pT relation.
$\Delta T = \Delta T_a + \Delta T_b + \Delta T_\epsilon$

It was only slightly different from the equation given by Berman and Swenson.
The three scales T_{48}, T_{55E} and T_{L55} are compared in fig. 16.

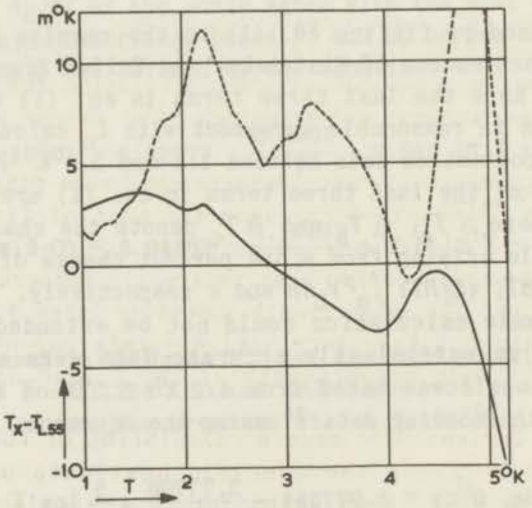

Fig. 16
Temperature differences between different scales.
— — — $T_{1948} - T_{L55}$
——— $T_{55E} - T_{L55}$

4. Development from 1955 to 1958

In January 1956 Ambler and Hudson [24] published results of their magnetic temperature measurements, their conclusion was that the measurements were more in agreement with T_{L55} than with T_{55E}. But later in 1956 they gave a complete discussion of all their measurements [25] and concluded that although there was a slight preference for T_{55E}, their results were not accurate enough to decide between T_{L55} and T_{55E}. A discussion of the two scales was given by Keller [56] in an article entitled "The Battle of the Millidegree". The quantity $d \ln p/d(1/T) + 5T/2$ was calculated both for T_{55E} and T_{L55}. It appeared that the second derivative d^2p/dT^2 for T_{55E} shows a discontinuity at the λ-point not in agreement with experimental data on the specific heat. For T_{L55} a discontinuity in the second derivative was found at 4.2°K, this is not to be expected from the thermodynamic data. The discontinuity in d^2p/dT^2 for T_{55E} resulted from the junction of the two empirical formulae on which T_{55E} was based, and it can be removed by changes in the scale of a few tenths of a millidegree. The discontinuity in d^2p/dT^2 for T_{L55} resulted from the junction of the thermodynamic calculation with equation (14) which was made in such a way that p and dp/dT were continuous. The discontinuity can also be removed by changes of less than one millidegree. Furthermore, it was Keller's opinion that the T_{55E} scale was superior to T_{L55} because of the uncertainties in the quantities that enter the thermodynamic calculation. The T_{L55} and T_{55E} scales were also discussed by Berman, Cooke and Hill [57]. Small deviations from T_{55E} were found by Sydoriak and Roberts [14] using their vapour pressure-temperature relation for ^{3}He and the data of Abraham, Osborne and Weinstock [34] on vapour pressures of ^{3}He and ^{4}He.

Some new measurements of thermodynamic data were published. Hill and Lounasmaa [58] measured the specific heat of liquid helium from 1.8 to 5.2°K. Fairbank, Buckingham and Kellers [59] made measurements of the specific heat in a small temperature region near the λ-point. The measurements showed no large discrepancies with older data but they were more accurate especially above 2.5°K. Kerr [60] made measurements of the liquid density from 1.2 to 4.2°K.

Van Dijk and Durieux [8,61] made a calculation of the change in T_{L55} when above 2.5°K the specific heat data of Hill and Lounasmaa were used. When using for L_0 the value of Erickson (59.564 joule/mole), the boiling point was 4.215°K.

In 1957 Clement [62] reported a thermodynamic calculation of the *pT* relation. The main differences with the calculation of T_{L55} were:

1. Above 1.8°K the specific heat data of Hill and Lounasmaa were used together with those of Fairbank, Buckingham and Kellers.
2. A third virial coefficiënt C was introduced in the calculation of ϵ.
3. L_0 was taken equal to 59.718 joule/mole instead of 59.50 joule/mole as in T_{L55}.
4. The liquid density was taken in accordance with the data of Kerr but this does not introduce any significant change.

The result was a scale that was very near to T_{55E}, the differences being smaller than the uncertainties in the thermodynamic quantities. The scale will be denoted here by $T_{Cl\text{-}th}$. (Temperature differences between this scale and T_{58} are shown in fig. 22).

The results of the thermodynamic calculations were discussed at a meeting at the National Bureau of Standards at Washington (July 30 - August 1, 1957) [63] and reported at the Madison Conference on Low Temperature Physics and Chemistry in August 1957. In Washington it was decided to try to make a new temperature scale as soon as possible with cooperation between the Naval Research Laboratory and the Kamerlingh Onnes Laboratory. It was decided that it was necessary to make a new study of all thermodynamic data entering into the calculation (L, B, C, V_L and C_L) old as well as new, and of direct measurements of the vapour pressure with the gas thermometer taking into due account data obtained from measurements on paramagnetic salts and with carbon thermometers. The boiling point of normal hydrogen would be taken as 20.377°K (for reference temperature in gas thermometer and magnetic thermometer calibrations), the boiling point of helium as 4.2155 ± 0.0015°K, the λ-point pressure as 37.80 mm Hg at 0°C (see the Appendix to this chapter). The pressure at the critical point would be taken as 1718 mm Hg at 0°C. For the constants R and i, $R = 8.31662$ joule/mole °K, $i = 12.2440$ cgs units would be used. A report of the Conference has been given by Brickwedde [63].

During the end of 1957 and the beginning of 1958 much work was done at the Naval Research Lab. and in Leiden to reevaluate all the available thermal and *pVT* date necessary for the calculation of the *pT* relation,

Some additional data on these quantities were published after the Washington Conference. Edeskuty and Sherman [64] and Edwards [65] measured the liquid density up to the boiling point. Their data were in between those of Kamerlingh Onnes and Boks used in T_{L55} and those of Kerr used in $T_{Cl\text{-}th}$. The temperature differences arising from differences in $\int_0^p V_L\, dp$ between T_{L55} and $T_{Cl\text{-}th}$ being at most 0.08 m°K the new data do not introduce any significant change in the scale. New data on the density of the saturated vapour were given by Edwards [66]. The density was deduced from the refractive index using the Lorenz-Lorentz equation. Also data on isotherms at 4.0°K and higher temperatures were given.

Analyses of all data on the virial coefficients were made by Clement [67] and by Van Dijk, Ter Harmsel and Van Rijn. Also the specific heat measurements of Hill and Lounasmaa were recalculated using the original calibration data of the carbon thermometers.

In January 1958 Dr. J.K. Logan came to the Kamerlingh Onnes Laboratory to analyse together with us the thermodynamic material. In March it appeared that it was not possible to complete the analysis before the session of the Advisory Committee for Thermometry in June in Sèvres and before the Kamerlingh Onnes Conference to be held in June in Leiden. Nevertheless it was desirable to arrive at a joint scale to replace T_{55E} and T_{L55} before that time.

In April 1958 a new scale was calculated by Clement, Logan and Swim, which they called T_α. This scale was intended to be an average between T_{55E} and T_{L55} in such a way that $d \ln p/d(1/T) - 5T/2$ had the shape that must be expected from thermodynamics. The scale was not published. For our further discussion it is sufficiently defined by fig. 17.

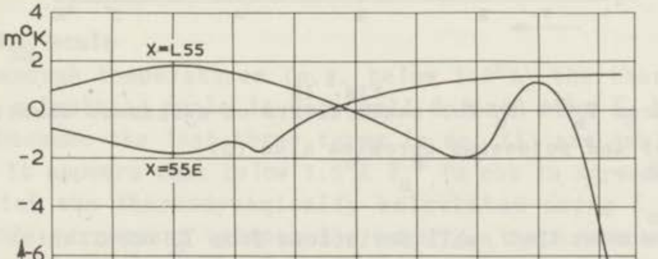

Fig. 17

Temperature differences $T_\alpha - T_X$, where X denotes the L55 and the 55E scales.

At that time the magnetic measurements described in Chapter II had been completed. It has been shown in Chapter II that deviations occurred when the results were compared with T_{L55} and T_{55E}. The measurements were also compared with T_{α}.

5. Comparison of magnetic temperatures with T_{α}

The same procedure was followed as described in Chapter II. For each series of measurements a magnetic temperature T_m^{α} was defined by the relation

$$n = A + B/(T_m^{\alpha} + \Delta) \qquad (15)$$

A, B and Δ were determined from the conditions that at the boiling point and in the neighbourhood of the λ-point $T_m^{\alpha} = T_{\alpha}$ and at the boiling point of hydrogen $T_m^{\alpha} - T_V = -18$ m°K. The results for manganese ammonium sulphate and potassium chromium alum are shown in fig. 18.

Fig. 18

Differences $T_m^{\alpha} - T_{\alpha}$ for measurements on manganese ammonium sulphate (o) and potassium chromium alum (□).

It can be seen that small deviations from T_{α} occur which are the same for manganese ammonium sulphate and for potassium chromium alum.

Because it appeared necessary to introduce a rather large Δ in the case of potassium chromium alum, it seemed to be worthwhile to investigate whether in Ambler and Hudson's data on methylammonium chromium alum [24, 25] a suitable Δ could be introduced. Again a T_m^{α} was defined with eq. (15). The measurements were only made in the helium region and therefore we determined the constants by taking $T_m^{\alpha} = T_{\alpha}$ at about 4.2, 3.3 and 2.2°K. (It followed from our measurements (see fig. 18) that at 3.3°K $T_m^{\alpha} = T_x$.) The results are given in fig. 19.

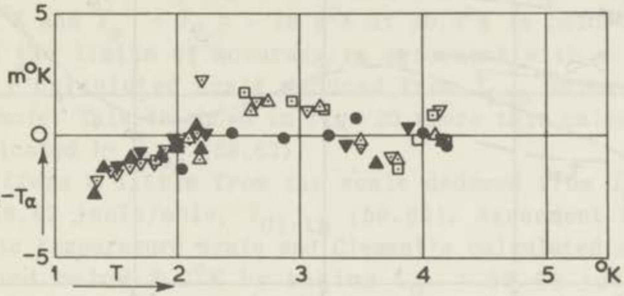

Fig. 19
Differences $T_m^{\alpha} - T_\alpha$ for methylammonium chromium alum (Ambler and Hudson).

The Δ introduced was 0.018°K. The results were in excellent agreement with ours. The data of Ambler and Hudson were especially valuable below the λ-point as the scatter of their data was smaller than that of our points. As a conclusion we may say that for all three salts small but approximately equal deviations occur from T_α. In fig. 20 a smooth curve is drawn giving the mean deviation from T_α for all magnetic measurements.

6. The T_{58} scale

At low enough temperatures (e.g. below 1.9°K) the thermodynamically calculated scale is very well defined when L_0 has been chosen because the last three terms in eq. (1) are small. From fig. 20 it appears that below 1.9°K T_m^{α} is not in agreement with T_{L55} which was thermodynamically calculated using L_0 = 59.50 joule/mole. Agreement between the magnetic temperature and the thermodynamically calculated scale cannot be obtained by changing only L_0, but can be obtained by changing L_0 and the magnetic temperature in an appropriate way.

The magnetic temperature can be changed by varying T_m at the calibration temperatures 20.4, 4.2 and 2.2°K. It can be derived from eq. (6) Ch. II that for small changes of the scale this results in a change in T_m [69]

$$\Delta T_m = a + bT_m + cT_m^2 \qquad (16)$$

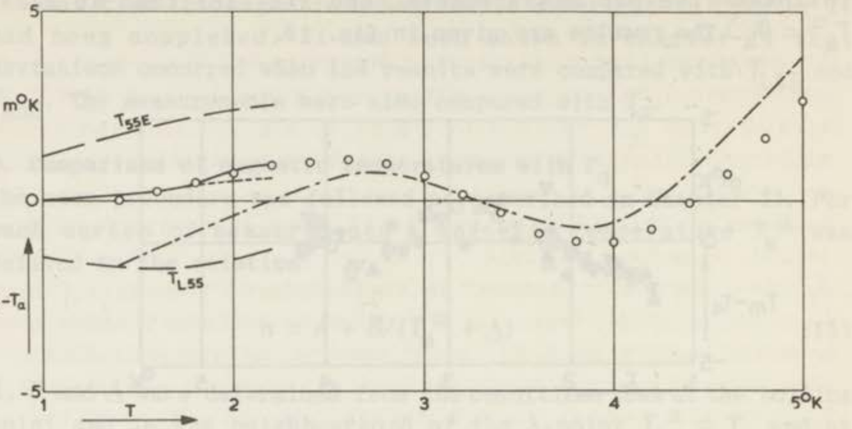

Fig. 20

Fitting of the magnetic temperature to the thermodynamically calculated temperature below the λ-point.

——— – ——— $T_m^{\alpha} - T_{\alpha}$

——————— T_{L55} (L_o=59.62) - T_a

— — — — $T_{Cl\text{-}th}$ (L_o=59.62) - T_a

○ ○ ○ ○ $T_m' - T_{\alpha}$

A change of T_m at 20.4°K within the limits of permissable changes in the hydrogen boiling point (see Ch. V) has only a minor influence on T_m at helium temperatures.

The change of the thermodynamically calculated scale due to a change of L_o, ΔT_{th}, consists of two parts: 1. The main part given by

$$\Delta T_{th_1} = \frac{\Delta L_o}{RT} \frac{d\ T}{d \ln p} \qquad (17)$$

2. A small effect arising from the term $\int_0^T S_L dT$.

When the scale changes, C_L changes too, and $\int_0^T S_L dT$ must be recalculated. For small changes of the scale this may be approximated by taking $\int_0^T S_L dT = \int_0^{T^*} S_L{}^* dT^*$ when T changes into T^*. In ref. 69 it is shown that this transformation holds for scale transformations of the form $T^* = T + cT$, in which c is a constant. Taking, for example, ΔL_o = + 0.10 joule/mole, ΔT_{th_1} = + 2.1 m°K and the effect from the transformation of the entropy integral - 0.17 m°K; the total change in T_{th} being + 1.9 m°K. ΔT_m and ΔT_{th} must be determined in such a way that T_m joins smoothly into T_{th} at low temperatures. This can be done by a calculation (see ref. 69) or by a graphical method using different ΔT_m and ΔT_{th} curves.

It appeared that a magnetic temperature T_m' defined by the conditions $T_m' - T_\alpha = 0.9$ m°K at 2.2°K and $T_m' - T_\alpha = -0.7$ m°K at 4.2°K and $T_m' - T_V = -18$ m°K at 20.4°K is below the λ-point within the limits of accuracy, in agreement with a thermodynamically calculated scale deduced from T_{L55} using $L_o = 59.62$ joule/mole. This is shown in fig. 20 where this calculated scale is indicated by T_{L55} (59.62).

T_m' differs a little from the scale deduced from T_{Cl-th} using $L_o = 59.62$ joule/mole, T_{Cl-th} (59.62). Agreement between the magnetic temperature scale and Clement's calculated scale can be obtained below 2.2°K by taking $L_o = 59.66$ joule/mole and $T_m'' - T_\alpha = 1.2$ m°K at 2.2°K, $T_m'' - T_\alpha = -1.0$ m°K at 4.2°K and $T_m'' - T_V = -18$ m°K at 20.4°K. The differences between T_m' and T_m'' are below 1 m°K.

The boiling point in the T_α scale was 4.2157°K and the temperature of the λ-point (37.80 mm Hg, 0°C) was 2.1711°K, thus these points in the T_m' scale are 4.2150 and 2.1720°K respectively.

A smooth scale was calculated on the basis of T_m' and T_{L55} (59.62). Use was made of the existing scales T_α and T_{L55} by making large plots of differences between the new scale defined by T_m' and T_{L55} (59.62) and T_α and T_{L55}. Smooth curves were drawn from which differences could be read with a precision of 10^{-6}°K. The procedure has been described in detail in ref. 69. A table of pressures and temperatures with intervals of 0.01°K was prepared. The smooth pT table with 0.01°K entries was discussed at an informal meeting at Leiden, June 13, 14 and 16, attended by F.G. Brickwedde, J.K. Logan (acting also for J.R. Clement), H.F. Stimson, H. van Dijk and M. Durieux. It was decided to present it to the Advisory Committee on Thermometry of the International Committee on Weights and Measures at its meeting in Sèvres, June 20 and 21, 1958, as the defining table for a new helium vapour pressure scale called the T_{58} scale [9,70].

It was further decided that, if adopted by the Advisory Committee, the scale would be expanded by Clement and Logan using an electronic computer to a table giving p at millidegree intervals. Also, a reverse table of T as a function of p would be made. Some auxiliary tables including a table of pressure-temperature derivatives and a table of differences between the 1958 scale and all formerly used scales would be prepared with the cooperation of the Naval Research Laboratory and the Kamerlingh Onnes Laboratory. Later on it was decided to ask the National Bureau of Standards in Washington to publish in its journal the

pT table with the inverted table and the auxiliary tables, together with an introduction by F.G. Brickwedde.
The Advisory Committee made the following recommendation in its session of June 20-21, 1958.
Le Comité Consultatif de Thermométrie,

ayant reconnu la nécessité d'établir dans le domaine des très basses températures une échelle de température unique,

ayant constaté l'accord général des spécialistes dans ce domaine de la physique,

recommande pour l'usage général l' "Échelle ^{4}He 1958", basée sur la tension de vapeur de l'hélium, comme définie par la table annexée (see table IV).

Les valeurs des températures dans cette échelle sont désignées par le symbole T_{58}.
The table defining T_{58} was distributed at the Kamerlingh Onnes Conference. It is given here as table IV. The International Committee on Weights and Measures approved the 1958 ^{4}He Scale of Temperatures at its meeting in Sèvres, September 29 to October 3, 1958. The publication in the Journal of Research of the National Bureau of Standards can be expected in February-March 1960.

7. Discussion of T_{58}

7a. Comparison with gas thermometer data

The measurements with the gas thermometer and isotherm measurements are fundamental for the scale. The new data will be mentioned here, the old have been discussed in ref. 27.
Fig. 21 gives a picture of recent measurements.
1. The gas thermometer measurements of Schmidt and Keesom at the boiling point. The gas thermometer was calibrated at the boiling point of normal hydrogen. The pressure of the gas was very low (0.7 mm Hg at 4.2°K) and was measured with a hot-wire manometer, which was kept at 77°K. In this way both the non-ideality correction and the correction for the thermomolecular pressure effect were kept small. At 4.2°K these corrections were 2 m$^{\circ}$K and 5 m$^{\circ}$K respectively. Schmidt and Keesom [71] arrived at an average value for the boiling point of 4.216°K using 20.381°K for the boiling point of normal hydrogen. Recalculated to 20.378°K the average is 4.215$_4$$^{\circ}$K. The points in fig. 21 are recalculated to 20.378°K. It may be remarked that this result was in very close agreement with the value 4.216°K which was given by Keesom in 1929.
2. The isotherm and gas thermometer measurements of Kistemaker and Keesom [72,22,23]. These were all relative to the boiling point

TABLE IV

Vapour pressure of ^{4}He. Unit 10^{-3}mm Hg at 0°C, $g = 980.665$ cm s^{-2}.

T	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
0.5	.016342	.022745	.031287	.042561	.057292	.076356	.10081	.13190	.17112	.22021
	.28121	.35649	.44877	.56118	.69729	.86116	1.0574	1.2911	1.5682	1.8949
	2.2787	2.7272	3.2494	3.8549	4.5543	5.3591	6.2820	7.3365	8.5376	9.9013
	11.445	13.187	15.147	17.348	19.811	22.561	25.624	29.027	32.800	36.974
	41.581	46.656	52.234	58.355	65.059	72.386	80.382	89.093	98.567	108.853
1.0	120.000	132.070	145.116	159.198	174.375	190.711	208.274	227.132	247.350	269.006
	292.169	316.923	343.341	371.512	401.514	433.437	467.365	503.396	541.617	582.129
	625.025	670.411	718.386	769.057	822.527	878.916	938.330	1000.87	1066.67	1135.85
	1208.51	1284.81	1364.83	1448.73	1536.61	1628.62	1724.91	1825.58	1930.79	2040.67
	2155.35	2274.99	2399.73	2529.72	2665.09	2805.99	2952.60	3105.04	3263.48	3428.07
1.5	3598.97	3776.32	3960.32	4151.07	4348.79	4553.58	4765.68	4985.18	5212.26	5447.11
	5689.88	5940.76	6199.90	6467.42	6743.57	7028.47	7322.31	7625.21	7937.40	8259.02
	8590.22	8931.18	9282.06	9643.02	10014.3	10395.9	10788.2	11191.2	11605.1	12030.1
	12466.1	12913.7	13372.8	13843.6	14326.1	14820.7	15327.3	15846.3	16377.7	16921.7
	17478.2	18047.7	18630.1	19225.5	19834.1	20455.9	21091.1	21739.7	22402.0	23077.9
2.0	23767.4	24470.9	25188.1	25919.2	26664.2	27423.3	28196.3	28983.2	29784.2	30599.1
	31428.1	32271.1	33128.0	33998.6	34882.8	35780.3	36690.9	37614.3	38550.2	39500.3
	40465.6	41446.6	42443.5	43456.5	44485.7	45531.3	46593.5	47672.5	48768.6	49881.8
	51012.3	52160.2	53325.8	54509.2	55710.5	56930.0	58167.8	59423.8	60698.8	61992.0
	63304.3	64635.2	65985.4	67354.8	68743.5	70152.0	71580.2	73028.1	74496.0	75984.2
2.5	77493.1	79022.2	80572.2	82142.9	83734.6	85347.2	86981.2	88636.7	90313.8	92012.6
	93733.4	95476.0	97240.8	99028.2	100838	102669	104525	106403	108304	110228
	112175	114145	116139	118156	120198	122263	124353	126465	128603	130765
	132952	135164	137401	139663	141949	144260	146597	148961	151349	153763
	156204	158671	161164	163684	166230	168802	171402	174028	176682	179364
3.0	182073	184810	187574	190366	193187	196037	198914	201820	204755	207719
	210711	213732	216783	219864	222975	226115	229285	232484	235714	238974
	242266	245587	248939	252322	255736	259182	262658	266166	269706	273278
	276880	280516	284183	287883	291615	295380	299178	303008	306871	310768
	314697	318659	322654	326684	330747	334845	338976	343141	347341	351575
3.5	355844	360147	364485	368860	373269	377714	382194	386710	391262	395849
	400471	405130	409825	414556	419324	424128	428968	433846	438760	443713
	448702	453729	458794	463897	469038	474218	479435	484691	489985	495317
	500688	506098	511547	517036	522564	528132	533739	539387	545075	550805
	556574	562383	568234	574126	580059	586034	592051	598110	604210	610352
4.0	616537	622764	629033	635345	641700	648099	654541	661026	667554	674125
	680740	687399	694103	700851	707643	714479	721360	728285	735255	742269
	749328	756431	763579	770772	778010	785294	792623	799999	807422	814893
	822411	829978	837592	845255	852966	860725	868533	876390	884296	892252
	900258	908313	916418	924573	932778	941033	949338	957693	966099	974556
4.5	983066	991628	1000239	1008905	1017621	1026390	1035213	1044087	1053014	1061995
	1071029	1080114	1089254	1098449	1107699	1117002	1126359	1135772	1145239	1154761
	1164339	1173972	1183662	1193407	1203209	1213066	1222981	1232955	1242983	1253069
	1263212	1273414	1283673	1293991	1304367	1314802	1325297	1335850	1346462	1357136
	1367870	1378662	1389516	1400429	1411404	1422438	1433533	1444690	1455911	1467191
5.0	1478535	1489940	1501409	1512940	1524535	1536192	1547912	1559698	1571546	1583458
	1595437	1607481	1619589	1631761	1644000	1656305	1668673	1681108	1693612	1706180
	1718817	1731521	1744290							

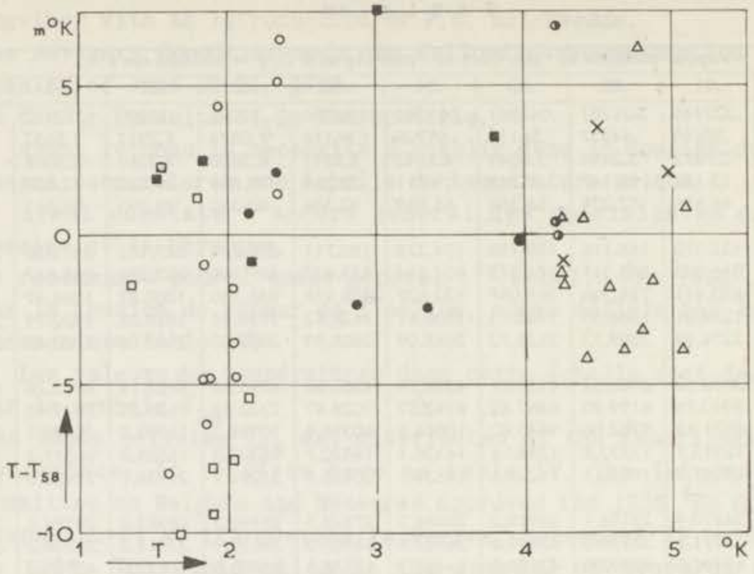

Fig. 21

Temperatures derived from gas thermometer and isotherm measurements compared with T_{58}.

◑ Schmidt and Keesom
○ Kistemaker and Keesom (isotherms)
□ Kistemaker (gas thermometer)
△× Berman and Swenson
● Keller (^{4}He)
■ Keller (^{3}He)

of helium. The isotherm points in fig. 21 are taken from a recalculation by Van Dijk using new data for the virial coefficients (see note on p. 63) and a correction for the hydrostatic pressure head at the boiling point, where necessary. A similar analysis made by Clement [73] led to results that were, in general, in agreement with Van Dijk's calculation within 2 m°K.

3. The gas thermometer measurements of Berman and Swenson [35,74]. The gas thermometer was calibrated at the boiling point of normal hydrogen. The data in the figure have been recalculated to 20.378°K. One series was relative to the boiling point of helium (indicated by crosses in fig. 21). The pressures in the gas thermometer at 4°K were about 4, 8 and 16 cm Hg. For a pressure of 4 cm Hg at 4°K the corrections for the non-ideality of the gas and for the thermomolecular pressure effect in the gas thermometer capillary were 23 m°K and 7 m°K respectively.

4. The isotherm measurements of Keller [36]. The temperature was obtained from the extrapolated isotherms. The amount of gas

in the gas thermometer was determined at room temperature. Keller's gas thermometer could be closed at low temperatures thus avoiding corrections for the dead space. Relatively wide capillaries could be used which made the correction for the thermomolecular pressure effect negligible. Measurements were made with ^{4}He and with ^{3}He gas. For the ^{4}He isotherms the result of a recalculation of Keller's isotherm data by Van Dijk and Ter Harmsel has been given.

7b. Comparison with magnetic temperatures

These are extensively discussed in the preceding sections. The results can also be seen from figs. 25, 26 and 27. It was shown that although three unknown constants appear in the equation for the magnetic temperature, the condition that T_m should smoothly join into the thermodynamically calculated scale below T_λ considerably restricts the choice of the constants.

7c. The carbon thermometer data

The carbon thermometer data were used in making the T_{55E} scale [44]. Because of the lack of a theoretical relation between the resistance and the temperature, it may be said that if the data are in agreement with T_{55E}, they are also in agreement with T_{58} since there is only a slight difference between the two scales without "sharp peaks".

7d. Thermodynamic calculations

In fig. 22 T_{58} can be compared with $T_{Cl\text{-}th}$, which is the latest complete thermodynamically calculated scale up to 4.5°K. In so far as T_{58} is based upon our magnetic measurements it can be remarked that any ΔT_m of the form given by eq. (16) can be added to the magnetic temperature. It may be estimated that if a magnetic temperature T_m was fitted to $T_{Cl\text{-}th}$ and to the hydrogen boiling point, small deviations between T_m and $T_{Cl\text{-}th}$ would arise but they would not exceed 1 m°K.

It may be mentioned that the rather steep decrease of T_{L55} between 3.8 and 4.2°K was due to the neglection of the third virial coefficient C.

Only one aspect of the thermodynamic calculations, namely that of using Berman and Poulter's [48] and Berman and Mate's [75] heat of vaporization data, will be treated in some detail because these data can easily be compared with T_{58}. Berman and Mate published their final results in 1958 [75] and compared them with T_{55E} and T_{L55}. A slightly different procedure will be followed here.

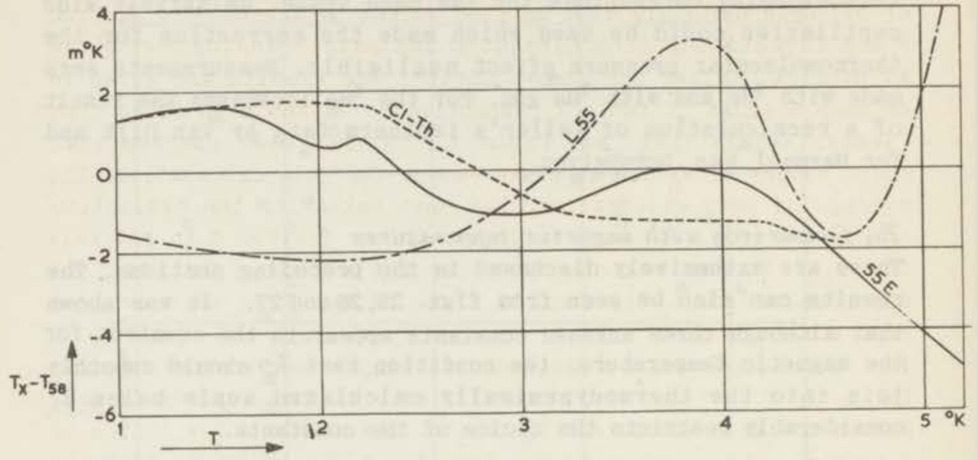

Fig. 22
Temperature differences T_X - T_{58} where X denotes different scales as indicated in the figure.

Eq. (8) has been used to calculate d ln p/d($1/T$). Smoothed values of L_a taken from Berman and Mate [75] are listed in table V.

TABLE V

Comparison of Berman and Mate's data on L_a with T_{58}.

T_{55E}	p	L_a	V_G	$\frac{B}{V_G}+\frac{C}{V_G{}^2}$		$-\frac{d \ln p}{d(1/T)}$		$\frac{\Delta d \ln p/d(1/T)}{d \ln p/d(1/T)}$
°K	mm Hg, 0°C	J/mole	cm^3/mole	Leiden	N.R.L.	(eq (8))	(T_{58})	°/oo
2.2	40.39	92.2	3215.2	-0.0538	-0.0549	11.723	11.639	7.2
2.4	63.30	93.6	2197.0	-0.0712	-0.0721	12.123	12.021	8.4
2.6	93.87	95.05	1572.0	-0.0904	-0.0910	12.569	12.486	6.6
2.8	133.2	96.5	1165.6	-0.1115	-0.1117	13.061	12.972	6.8
3.0	182.4	97.8	888.7	-0.1341	-0.1340	13.580	13.461	8.8

The term $B/V_G + C/V_G^2$ has been calculated in two ways: 1. From B and C resulting from the analysis of Van Dijk and Ter Harmsel of pVT data using for B the adopted values by Keesom [76]*. 2. From B and C resulting from Clement's analysis [67] using for B the Kilpatrick, Keller and Hammel data**. The results are given in columns 5 and 6 of table V respectively. V_G has been taken from Clement's data (ref. 44, table E). It has been checked that these values of V_G are accurate enough for this calculation. The average of both calculations has been taken for the evaluation of $d \ln p/d(1/T)$ (column 7 table V). Column 8 gives $d \ln p/d(1/T)$ for T_{58}. It can be seen from the table that-$d \ln p/d(1/T)$ calculated from L_a is about 7.6°/oo higher than that derived from the T_{58} scale.

The calculation was not extended to higher temperature because the influence of the virial coefficients becomes rapidly larger. Berman and Mate state that L_a is accurate within a few tenths of a percent. The accuracy of the term $1 + B/V_G + C/V_G^2$ is probably ± 0.003. The better agreement between columns 5 and 6 in table V may be accidental. The difference in $d \ln p/d(1/T)$ of 7.6°/oo exceeds somewhat the estimated experimental accuracy of the data. It can be remarked that the difference between $d \ln p/d(1/T)$ calculated from L_a and taken from $T_{Cl\text{-}th}$ is of the order of 4.2 °/oo. This difference is within the estimated accuracy of the data.

7e. Concluding remarks

Summing up, we may say that T_{58} is in good agreement with most available data. It is especially reassuring that at the boiling point the data of Keller and of Berman and Swenson and Schmidt and Keesom's average value were in such a good agreement [77]. In this thesis much stress has been laid on the contribution of magnetic temperature measurements in establishing T_{58}, but the scale can be considered as being based upon gas thermometer, magnetic thermometer and carbon thermometer measurements as well as upon thermodynamic calculations.

The probable accuracy of the T_{58} scale is ± 2 m°K between 1 and 4.5° and ±3 m°K between 4.5 and 5.2°K in the temperature and ± 3°/oo in dp/dT.

---

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

$$C = \left(\frac{5000}{T} - \frac{4.86 \times 10^6}{T^5}\right) \frac{\text{cm}^6}{\text{mole}^2}$$

** B from ref. 52

$$C = \left(\frac{1500}{\sqrt{T}} - \frac{7.5 \times 10^6}{T^7}\right) \frac{\text{cm}^6}{\text{mole}^2}$$

We will make a remark about the smoothness of T_{58}. Due to the limited time in 1958 when T_{58} was calculated some "roughness" remained in the defining table: the second differences at about 3 and 4.2°K are not completely smoothed. It is not likely that this will give any trouble for users of the T_{58} scale. The "roughness" is illustrated in fig. 23 where the differences have been plotted between T_γ and T_{58}, T_γ being a smooth scale. To avoid confusion we wish to state that fig. 23 is not at all meant as a correction to be used with T_{58}.

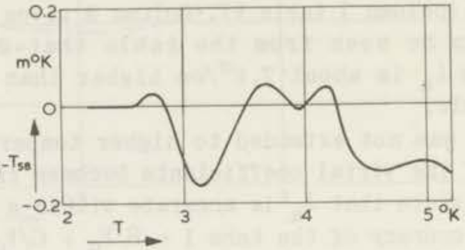

Fig. 23

Temperature differences $T_\gamma - T_{58}$ as a function of T.

Appendix: The λ-point pressure

We made some measurements to determine the λ-point pressure [78]. These consisted in warming up, or cooling down, a vessel containing liquid helium while measuring its vapour pressure. A discontinuity in the vapour pressure versus time curve indicated the λ-point. Part of the analysis was made by Mr. H. ter Harmsel.

Three kinds of experiments were made:

1. At first an apparatus was used similar to the one described in Chapter II for the magnetic temperature measurements. The average value found for p_λ was 37.81 mm Hg at 0°C.
2. Secondly, a cell containing some liquid helium isolated from the bulk helium was used. A phosphor bronze and a carbon thermometer were placed in the cell. The λ-point passage could be detected from the discontinuities in the pressure and the resistance curves when warming up or cooling down the cell. Fig. 24 gives the result of one series. The average value of p_λ was 37.78 mm Hg at 0°C.
3. Finally, measurements were made by warming up the helium in the dewar itself. A carbon thermometer was placed in the dewar. The value found for p_λ was 37.79 mm Hg at 0°C.

Based on our experiments alone we derive an average of 37.79

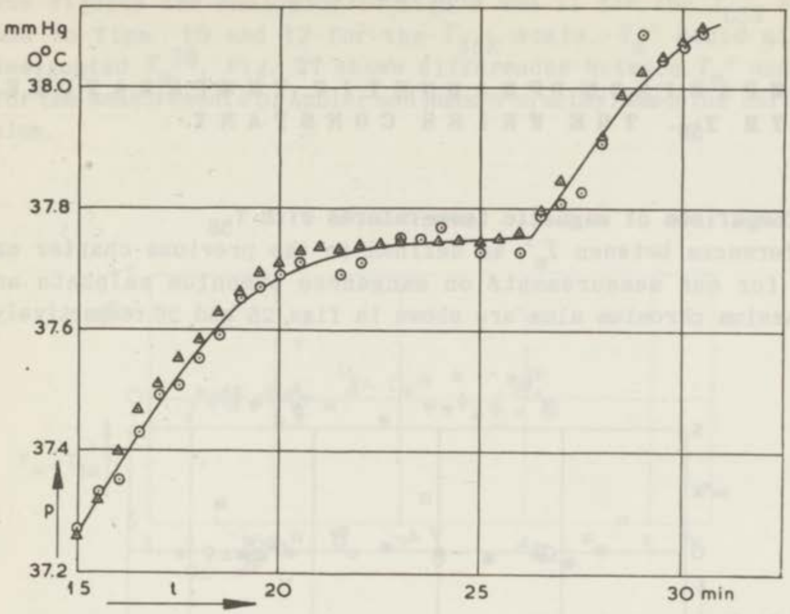

Fig. 24

Measurement of the λ-point pressure.
○ pressure
△ phosphor bronze thermometer

± 0.03 mm Hg at 0°C for the λ-point pressure.

The following data on the λ-point pressure were reported by others:

Long and Meyer	37.96 mm Hg at 0°C
Erickson and Roberts [21]	37.91 mm Hg at 0°C
Dash and Taylor [80]	37.86 mm Hg at 0°C
Winkel [81]	37.8 mm Hg at 0°C

All these values are lower than the value 38.3 mm Hg at 0°C given by Keesom and Schmidt in 1937 (ref. 76, p.225).

As mentioned in section 4 the average chosen at the Washington Conference in 1957 was 37.80 mm Hg at 0°C.

CHAPTER IV

COMPARISON OF MAGNETIC TEMPERATURES WITH T_{58}. THE WEISS CONSTANT.

1. Comparison of magnetic temperatures with T_{58}

Differences between T_m' as defined in the previous chapter and T_{58} for our measurements on manganese ammonium sulphate and potassium chromium alum are shown in figs. 25 and 26 respectively.

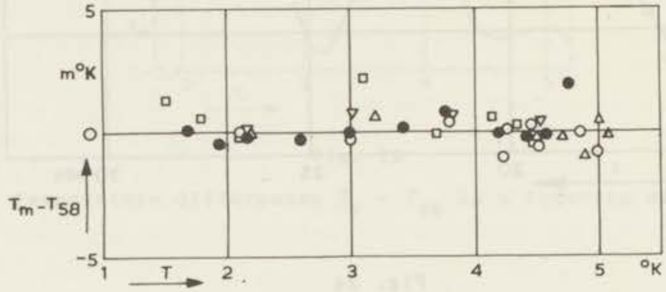

Fig. 25

Differences between the magnetic temperature T_m' and T_{58} for manganese ammonium sulphate. Measurements on different days are indicated as in fig. 9, Ch. II.

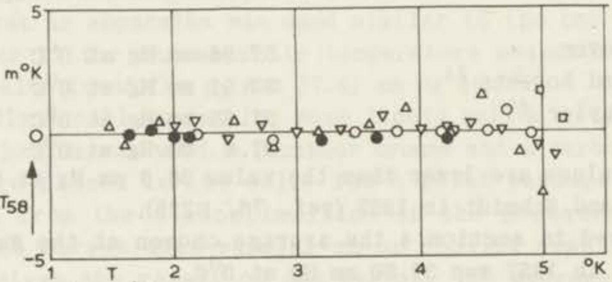

Fig. 26

Differences between the magnetic temperature T_m' and T_{58} for potassium chromium alum. Measurements on different days are indicated as in fig. 11, Ch. II.

The figures are analogous to figs. 9 and 11 for the T_{L55} scale and to figs. 10 and 12 for the T_{55E} scale. T_m' could also be designated T_m^{58}. Fig. 27 shows differences between T_m' and T_{58} for the measurements of Ambler and Hudson on methylammonium chromium alum.

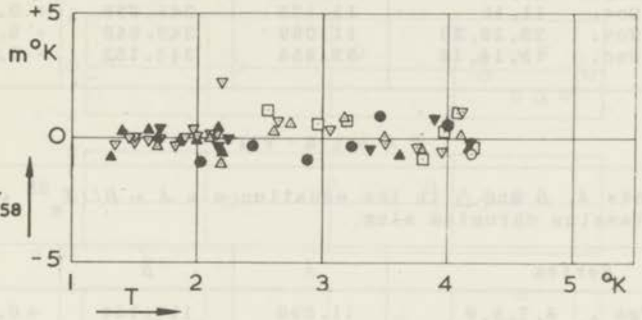

Fig. 27

Differences between the magnetic temperature T_m' and T_{58} for methylammonium chromium alum (Ambler and Hudson).

So far the results of series IV on manganese ammonium sulphate (see table II) have not been discussed. They were used to obtain information on the hydrogen pT relation and were analysed as follows: T_m^{58} was defined for series IVA (Nov. 28, 29) in the usual way by taking $T_m^{58} = T_{58}$ at 4.2 and 2.2°K and $T_m^{58} - T_V = -18$ m°K at 20.4°K. Constants A, B and Δ were obtained. For series IVB (Dec. 13, 14, 18) T_m^{58} was defined using $T_m^{58} = T_{58}$ at 4.2°K, $T_m^{58} - T_V = -18$ m°K at 20.4°K and using the Δ of series IVA, because series IVB was not extended to the λ-point and it appeared from series I that Δ did not change much when the salt was not removed from the dewar but was kept at nitrogen temperatures between the measurements (see table VI). The use of the value of Δ derived from series IVA was confirmed, moreover, by the agreement between T_m^{58} and T_{58} at 5.1°K on December 13 (see fig. 28g). Differences between T_m^{58} and T_V for the measurement of December 18 will be given in Chapter V.

Numerical values of the constants A, B and Δ for the different series with manganese ammonium sulphate (using T_{58}) are listed in table VI. The constants for potassium chromium alum are given

TABLE VI

Constants A, B and Δ in the equation $n = A + B/(T_m^{58} + \Delta)$ for manganese ammonium tuttonsalt.

Series			A	B	Δ
IA	May	14,17	11.287	346.195	+ 0.0134
IB	May	24,28	11.272	346.083	+ 0.0138
IC	June	6, 7	11.287	345.119	+ 0.0188
II	Sept.	25,27	11.063	344.118	- 0.0790
III	Oct.	11,15	11.176	345.288	+ 0.0317
IVA	Nov.	28,29,30	11.059	343.849	- 0.0430
IVB	Dec.	13,14,18	13.854	344.152	- 0.0430

TABLE VII

Constants A, B and Δ in the equation $n = A + B/(T_m^{58} + \Delta)$ for potassium chromium alum.

Series			A	B	Δ
IA	Feb .	6,7,8,9	11.090	117.154	+0.0383
IB	Feb .	17,18,19,21	11.095	117.007	+0.0347
IIA	March	12,13,14	11.065	116.594	+0.0359
IIB	March	19,20,21	11.059	116.708	+0.0359
III	March	27,28,29	10.995	114.096	+0.0350

in table VII. Differences between T_m' and T_{58} for each series are given in fig. 28 for manganese ammonium sulphate and in fig. 29 for potassium chromium alum. In these two figures all points given in tables II and III are indicated; in the combined graphs such as figs. 25 and 26 some points in the same series have been averaged. For manganese ammonium sulphate quite different values for the Weiss constant Δ were found when the salt sample had been removed from the cryostat between series. However, the Weiss constant for potassium chromium alum was nearly the same for different positions of the crystal in agreement with the cubic symmetry. The average of series I, II and III is $\Delta = 0.0356^{\circ}$K. The value of Δ depends on the fixed points used for defining the magnetic temperature. Using T_m^{L55} the value of Δ is 0.0066°K larger than for T_m^{58} and for T_m^{55E} it is 0.0028°K smaller.

The accuracy of the value 0.0356°K found for the Weiss constant of potassium chromium alum is probably $\pm$ 3 m$^{\circ}$K for uncertainties in the helium and hydrogen temperature scales and $\pm$ 6 m$^{\circ}$K in total.

Different values for the Weiss constant for a manganese ammonium sulphate crystal depending on its orientation with respect to

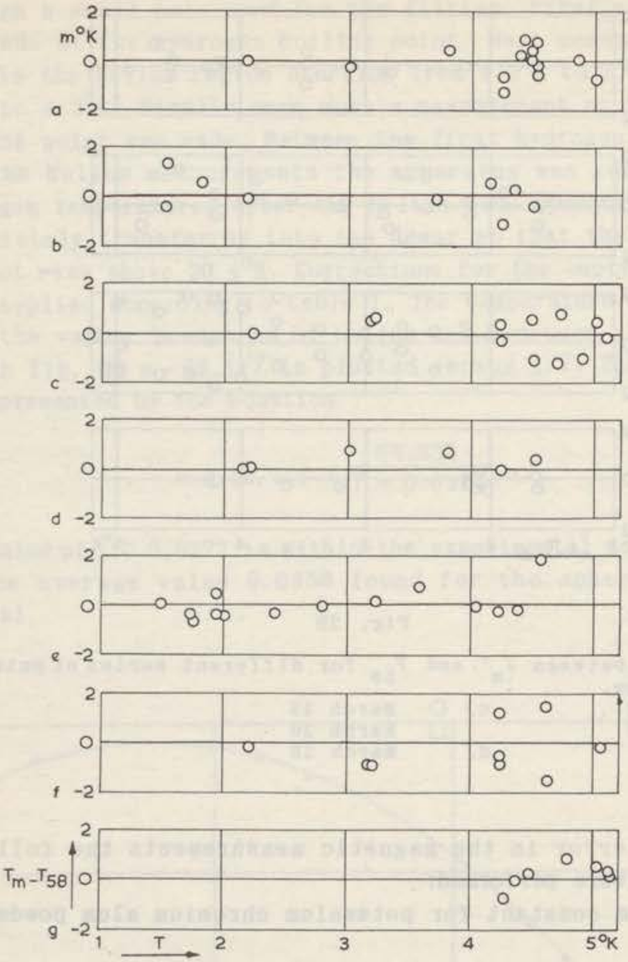

Fig. 28

Differences between T_m' and T_{58} for different series of manganese ammonium sulphate.

a. May 14
b. May 24
c. June 6
d. Sept. 27
e. Oct. 11
f. Nov. 28
g. Dec. 13

the magnetic field can be expected from the electric splitting of the magnetic levels in this salt [82].

For potassium chromium alum the value of Δ was much larger than expected [17]. To see if this could arise from an unexpected

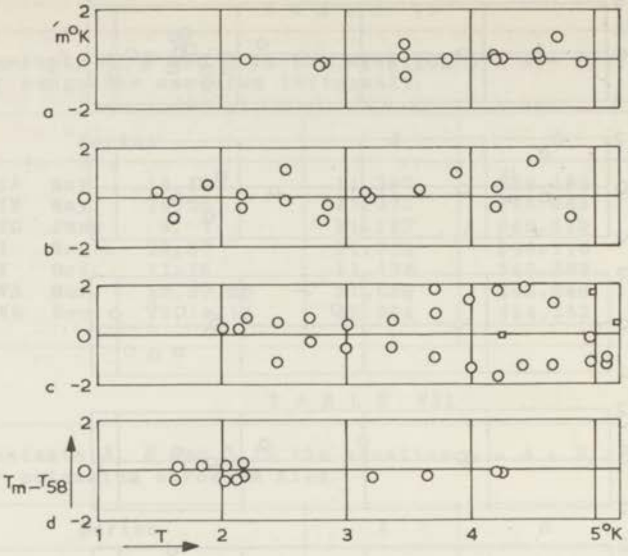

Fig. 29

Differences between T_m' and T_{58} for different series of potassium chromium alum.

a. Feb . 7
b. Feb . 18
c. ○ March 13
□ March 20
d. March 28

systematic error in the magnetic measurements the following experiments were performed:

1. The Weiss constant for potassium chromium alum powder was determined.
2. The Weiss constant for a single crystal of methylammonium chromium alum was determined.
3. The Weiss constant for a single crystal of potassium chromium alum was measured in a coil system of entirely different dimensions than the one described in Chapter II.

These measurements will be described in sections 2, 3 and 4. In section 5 the theoretical equations for the susceptibility of the chromium alums will be discussed.

2. Potassium chromium alum powder

A hollow glass sphere was filled with small crystals of potassium chromium alum and placed in the thermometer vessel Th (see fig. 2). The measurements were carried out in the way described in Chapter II. The condensed helium could enter the sphere through a small hole used for the filling. First a measurement was made at the hydrogen boiling point. Next measurements were made in the helium region starting from 4.2°K to 1.5°K and then back to 4.2°K. Finally, once more a measurement at the hydrogen boiling point was made. Between the first hydrogen measurement and the helium measurements the apparatus was kept at liquid nitrogen temperature. After the helium measurements hydrogen was immediately transferred into the dewar so that the temperature did not rise above 20.4°K. Corrections for the empty coil effect were applied according to table I. The temperature was obtained from the vapour pressures of helium and hydrogen using T_{58} and T_V. In fig. 30 n - 66.1/T is plotted versus 1/T. The data could be represented by the equation

$$n = 13.717 + \frac{66.853}{T + 0.0377} \qquad (1)$$

The value of Δ = 0.0377 is within the experimental accuracy equal to the average value 0.0356 found for the spherical single crystal.

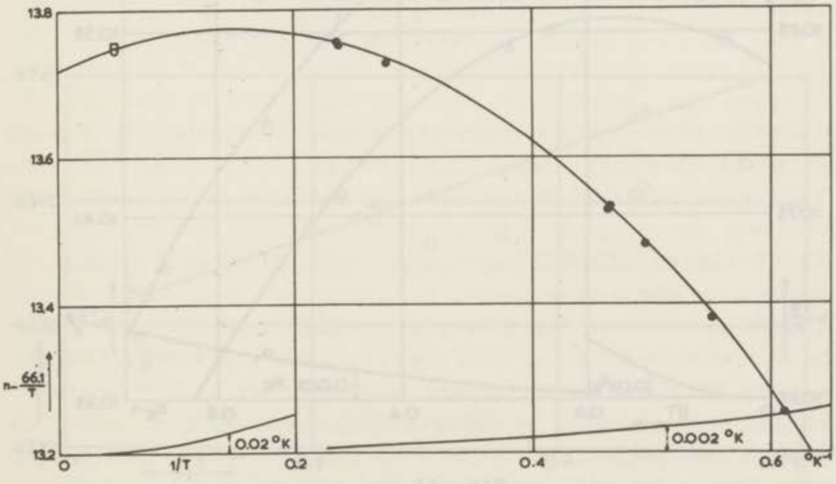

Fig. 30

n - 66.1/T versus 1/T for potassium chromium alum powder. The curve drawn has been calculated from eq. (1).

3. Methylammonium chromium alum crystal

A spherical crystal* was used that had been used previously in our temperature measurements with the self inductance method. Afterwards it was broken into three pieces. The pieces were glued together and the series of measurements hydrogen-helium-hydrogen was made. Measurements were made at 227 and 120 Hz. The data could be represented by the equations:

$$n = 10.859 + \frac{79.468}{T + 0.013} \ (227\ \mathrm{Hz}) \tag{2}$$

$$n = 10.525 + \frac{79.352}{T + 0.013} \ (120\ \mathrm{Hz}) \tag{3}$$

This is shown in fig. 31 where the two lines drawn represent eqs. (2) and (3). The value of $\Delta = 0.013^{\circ}\mathrm{K}$ was determined mainly by

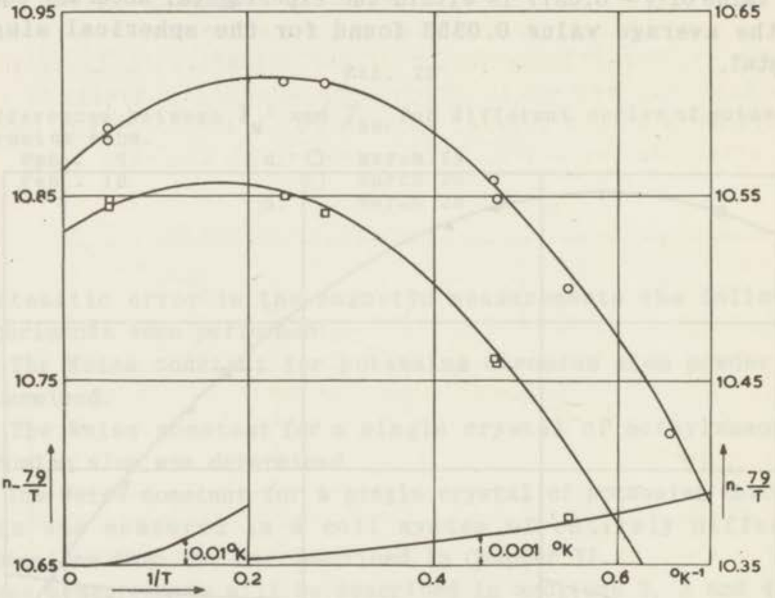

Fig. 31

$n - 79/T$ versus $1/T$ for methylammonium chromium alum. The circles, the upper curve and the left hand scale apply to measurements at 227 Hz. The lower curve and the right hand scale to 120 Hz.

---

* Our thanks are due to Dr. R.P. Hudson of the National Bureau of Standards (Washington) who kindly placed the crystal at our disposal.

fitting eq. (2) to the points at 20.4, 4.2 and 2.2°K because these were considered to be the most accurate ones. It appeared that eq. (3) with the same value of Δ also represented the data at 120 Hz. Before these measurements were made we found $\Delta = 0.017$°K from Ambler and Hudson's data in the helium region (see Ch. III). The difference is within the experimental accuracy. As an average we find $\Delta = 0.015$°K for a sphere of methylammonium chromium alum.

4. Potassium chromium alum crystal*

The measurements were made with the coil system used by Van der Marel and Van den Broek (see ref. 29). It was essentially the same as the one we used but the dimensions were quite different. The secondary coil in which the salt was located was 19 mm in diameter and 35 mm long.

The secondary coil was wound on a glass tube that was open at its lower end so that the crystal was in direct contact with the bulk helium. The pressures were measured at the bath and corrections for the hydrostatic head were applied. The crystal was the same as used for the measurements described in Chapter II. The filling factor of the secondary coil was much less than for our coils which were specially designed for measurements with a sphere, so a large influence of the empty coil effect was expected. This proved to be the case. Fig. 32

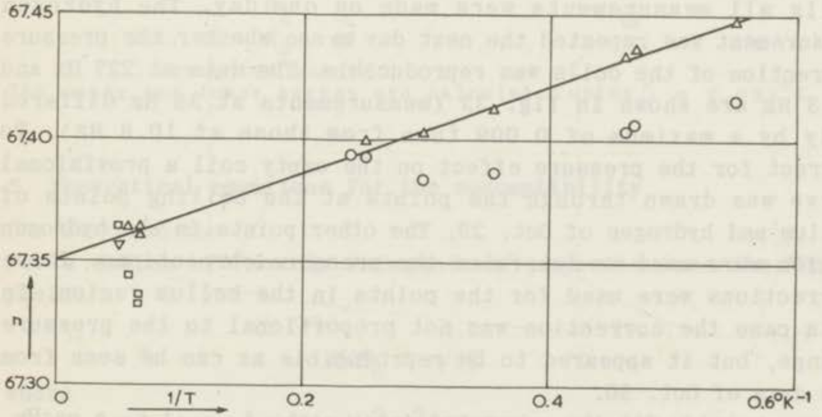

Fig. 32

Empty coil measurements.
∇ H_2 ○ He □ H_2
△ corrected points

---

* These measurements were made in cooperation with Dr. L.C. van der Marel, Mr. J. van den Broek and Mr. A.R. Miedema.

shows the results of a complete series of empty coil measurements. All measurements were made on one day. The measuring frequency was 227 Hz.

From the data the following procedure suggested itself. A provisional straight line was drawn through the points at the hydrogen and helium boiling points. The other points in the hydrogen region were shifted to this line. It appeared that this could be done by applying a correction proportional to the difference between the pressure in the dewar at each temperature and one atmosphere. The same correction was applied for the points in the helium region. The corrected points lay within the experimental accuracy on a straight line. Apparently there was a combined influence of the temperature and the pressure on the inductance of the coils. It may be mentioned that all coils were wound on open tubes. The pressure effect is different from the one described in Chapter II, when pressure differences occurred between the inner vessel and the dewar.

When we started the measurements with this coil system a pressure correction was found which had the reverse sign compared with the correction found above. After that the glass tube that carried the coils broke and was sealed anew.

A complete series of measurements, hydrogen-helium-hydrogen, was made with the salt sample. To avoid errors due to changes of the coils all measurements were made on one day. The hydrogen measurement was repeated the next day to see whether the pressure correction of the coils was reproducible. The data at 227 Hz and 10.8 Hz are shown in fig. 33 (measurements at 36 Hz differed only by a maximum of 0.009 turn from those at 10.8 Hz). To correct for the pressure effect on the empty coil a provisional curve was drawn through the points at the boiling points of helium and hydrogen of Oct. 29. The other points in the hydrogen region were used to determine the pressure corrections. These corrections were used for the points in the helium region. In this case the correction was not proportional to the pressure change, but it appeared to be reproducible as can be seen from the data of Oct. 30.

It was tried to fit the corrected data with a Δ equal to 0.035°K. The two curves in fig. 33 are calculated from $n = A + B/(T + 0.035)$. They represent the corrected points within the limits of accuracy. Obviously these measurements cannot be considered as an accurate determination of Δ, but in any case the result is not in contradiction to the results with the coil system described in Chapter II.

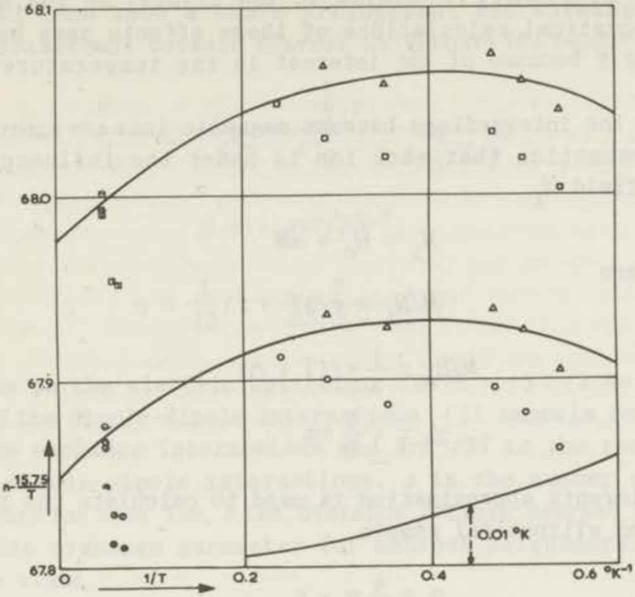

Fig. 33

n - 15.75/T versus 1/T for potassium chromium alum.

		227 Hz	10.8 Hz
Oct. 29:	H_2	⊖	⊟
	He	○	□
	H_2	⦶	◫
Oct. 30:	H_2	●	

△ corrected points

The upper and lower curves are calculated using Δ = 0.035°K.

5. Theoretical equations for the susceptibility

5a. Introduction

For a system of "nearly independent" magnetic ions the theory yields

$$M/H_0 = \tau/3T \tag{4}$$

where

$$\tau = Ng^2\mu_B{}^2J(J+1)/k \tag{5}$$

N = number of ions per unit of volume, g = Landé's splitting factor, μ_B = Bohr magneton, J = total magnetic quantum number and k = Boltzmann's constant, M and H_0 have been defined in Chapter II. In crystals deviations from eq. (4) can be expected arising from the interactions between the magnetic ions and the influence of electric fields in the crystal on the magnetic ions. Theoretical calculations of these effects have been made particularly because of the interest in the temperature region below 1°K.

Sometimes the interactions between magnetic ions are approximated by the assumption that each ion is under the influence of an internal field H_i

$$H_i = H_0 + \alpha M \tag{6}$$

In this case

$$M/H_i = \tau/3T \tag{7}$$

and thus

$$M/H_0 = \frac{1}{3}\tau/(T + \Delta) \tag{8}$$

where

$$\Delta = -\frac{1}{3}\tau\alpha \tag{9}$$

When the Lorentz approximation is used to calculate the internal field in an ellipsoidal sample

$$\alpha = \frac{4}{3}\pi - \epsilon \tag{10}$$

in which ϵ is the demagnetizing factor of the sample. For a sphere

$$\epsilon = \frac{4}{3}\pi \quad \text{and} \quad \Delta = 0 \tag{11}$$

More rigorous calculations have been made by Van Vleck and others [84,85,86]. In the first place, the crystalline electric field in salts of the iron group causes the quenching of the orbital momentum so that J in eq. (5) has its spin-only value, S. Secondly, there will be, in general, small splittings of the spin-levels. If the magnitude of the splittings be known (e.g. from paramagnetic resonance experiments) the influence on the susceptibility can be calculated. Van Vleck represents the interaction energy between magnetic ions by

$$w_{ij} = \frac{1}{r_{ij}^{3}}\left[(1 + v_{ij})(m_i \cdot m_j) - \frac{3(m_i \cdot r_{ij})(m_j \cdot r_{ij})}{r_{ij}^{2}}\right] \tag{12}$$

where r_{ij} is the distance between the ions and m_i the magnetic moment, v_{ij} accounts for the exchange energy. The calculation of the susceptibility was carried out by Van Vleck [84] by rigorous quantum mechanical methods. The result was given as a series expansion of which the first few terms were calculated. If the magnetic ions have a cubic arrangement and exchange is only taken into account between nearest neighbours the result is [84,17]

$$\frac{M}{H_0} = \frac{\frac{1}{3}\gamma\tau}{T - (\frac{4}{3}\pi - \epsilon)\frac{\tau}{3} - \theta + \frac{4}{3}\eta\frac{\tau^2}{T}} \tag{13}$$

with:

$$\theta = - z v\tau/3Nr^3 \tag{14}$$

$$\eta = \frac{1}{12}(1 + \frac{3}{8S(S + 1)})Q \tag{15}$$

γ is due to the electric splitting, $(4\pi/3 - \epsilon)\tau/3$ to the first order of the dipole-dipole interactions (it cancels for a sphere), θ to the exchange interactions and $4\eta\tau^2/3T$ to the second order of the dipole-dipole interactions. z is the number of nearest neighbours for each ion, r the distance between nearest neighbours and v the exchange parameter for nearest neighbours. $Q = 14.4$ for the alums.

5b. *The chromium alums*

The crystal structure of the chromium alums is well known. The Cr ions lie on a face-centered cubic lattice. There are four different kinds of Cr ions in the unit cell with their trigonal axes along the body diagonals of the cube. The ground state $S = 3/2$ is split by the trigonal field into two doublets $S_z = \pm \frac{1}{2}$ and $S_z = \pm 3/2$. The factor γ in eq. (13) is given by

$$\gamma = \frac{3 + 4x + (3 - 4x)e^{-1/x}}{5(1 + e^{-1/x})} \tag{16}$$

where $x = kT/\delta$ and δ is the energy difference between the two levels. Eq. (16) holds for a powder, but due to the averaging over the four kinds of ions it also holds for all directions of a single crystal. δ has been determined by paramagnetic resonance. For methylammonium chromium alum $\delta/k = 0.255^{\circ}$K [87]. In potassium chromium alum the structure below 90°K becomes so distorted that the ions are no longer in similar environments and three different lines have been found giving $\delta/k = 0.39$, 0.22 and 0.05°K [88]. It follows from measurements of the susceptibility below 1°K that the lowest level is $S_z = \pm 3/2$. The relative abundance of the three splittings in potassium chromium alum was assumed to be 32%, 42% and 26% by Beun, Miedema and Steenland[89], this being in agreement with the spectral intensities of the lines, specific heat data above 1°K and the entropy versus temperature relation down to 0.03°K.

Recently Miss O'Brien [86] analyzed the susceptibility of the chromium alums for the ideal cubic structure. Her theory applies in particular to the case of methylammonium chromium alum. The calculation was an extension of Van Vleck's calculation in so far as that the influence of the electric field splitting on the interactions between the ions was taken into account. Due to the crystalline electric field the average magnetic moment of the ions in each sublattice is bent a little towards the direction of its trigonal axis. This has a small effect on the dipole-dipole and exchange interactions between the ions. For a sphere Miss O'Brien finds a small contribution to the susceptibility from the first order of the dipole-dipole interactions *

$$\Delta\chi = -\,0.78\left(\frac{\tau}{T}\right)^2 \frac{2\sqrt{2}}{225}\left[3 - 2x\,\frac{1 - e^{-1/x}}{1 + e^{-1/x}} - \frac{4e^{-1/x}}{1 + e^{-1/x}}\right]^2 \qquad (17)$$

Because $\Delta\chi/\chi$ and $1-\gamma$ are small compared to one, one may write for a sphere, combining eqs. (13) and (17)

$$\frac{M}{H} = \frac{\tau/3}{T\left[1 + (1-\gamma) - \dfrac{\theta}{T} + \dfrac{4}{3}\eta\dfrac{\tau^2}{T^2} - \dfrac{\Delta\chi\cdot 3T}{\tau}\right]} \qquad (18)$$

The magnitudes of the terms $1-\gamma$, $4\eta\tau^2/3T^2$ and $\Delta\chi(3T/\tau)$ for methylammonium chromium alum are indicated in fig. 34. (δ/k = 0.255°K and τ = 0.0189°K [17]). It appears that to a good approximation

$$1 - \gamma = 0.00216/T^2 \qquad (19)$$

and

$$4\eta\tau^2/3T^2 = 0.00063/T^2 \qquad (20)$$

The term $\Delta\chi(3T/\tau)$ is negligible above 0.5°K. In this case one

---

* A typographical error occurred in the original publication (private communication from Dr. J.A. Beun).

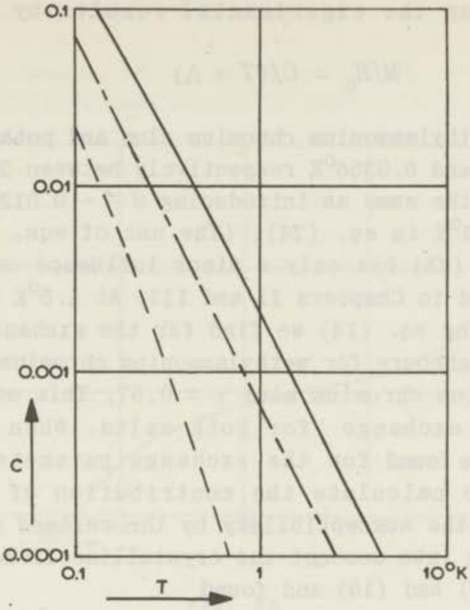

Fig. 34

The magnitude of the correction terms in eq. (18) versus temperature.

——————— $c = 1 - \gamma$

——·——·—— $c = 4\eta\tau^2/3T^2$

—— —— —— $c = -\Delta\chi(3T/\tau)$

obtains for a spherical crystal of methylammonium chromium alum

$$\frac{M}{H_0} = \frac{\tau/3}{T + 0.00279/T - \theta} \tag{21}$$

Taking into account the three splittings mentioned above one finds for potassium chromium alum

$$1 - \gamma = 0.00231/T^2 \tag{22}$$

and using $\tau = 0.0204^\circ\mathrm{K}$

$$4\eta\tau^2/3T^2 = 0.0073/T^2 \tag{23}$$

and thus

$$\frac{M}{H_0} = \frac{\tau/3}{T + 0.00304/T - \theta} \tag{24}$$

When describing the experimental results by the equation

$$M/H_0 = C/(T + \Delta) \tag{25}$$

we found for methylammonium chromium alum and potassium chromium alum $\Delta = 0.015$ and 0.0356°K respectively between 20.4 and 1.4°K. This is nearly the same as introducing $\theta = -0.012^\circ$K in eq. (21) and $\theta = -0.033^\circ$K in eq. (24). (The use of eqs. (21) and (24) instead of eq. (25) has only a minor influence on the magnetic temperature used in Chapters II and III. At 1.5°K the difference is 0.3 m°K.) Using eq. (14) we find for the exchange parameter v for nearest neighbours for methylammonium chromium alum $v = 0.22$ and for potassium chromium alum $v = 0.57$. This means an antiferromagnetic exchange for both salts. When these rather large values were found for the exchange parameters it seemed interesting to calculate the contribution of the exchange interaction to the susceptibility by the refined method of Miss O'Brien (taking into account the crystalline field). We started from her eqs. (9) and (10) and found

$$\Delta\chi_{\mathrm{exch}} = -\frac{4vN\mu_B^{\,4}}{9r^3k^2T^2}\left[3(P + 2Q)^2 - 2(P - Q)^2\right] \tag{26}$$

where

$$P = \frac{9 + e^{-1/x}}{1 + e^{-1/x}}, \quad Q = \frac{4e^{-1/x} + 6x(1 - e^{-1/x})}{1 + e^{-1/x}} \tag{27}$$

This means, that θ in eq. (18) has to be replaced by an effective θ

$$\theta_{\mathrm{eff}} = \Delta\chi_{\mathrm{exch}}(3T^2/\tau) \tag{28}$$

Substituting eq. (26) in eq. (28) we obtain, using eq. (14)

$$\theta_{\mathrm{eff}} = g(T)\,\theta \tag{29}$$

with

$$g(T) = \frac{1}{675}\left[3(P + 2Q)^2 - 2(P - Q)^2\right] \tag{30}$$

Fig. 35 shows the function $g(T)$ for $\delta/k = 0.255^\circ$K. As could be expected $g(T) = 1$ for $T \gg \delta/k$. The low temperature limit of $g(T)$ equals 9/75. From fig. 35 it follows that θ_{eff} does not change much for temperatures above 0.3°K. The calculation with $\delta/k = 0.255^\circ$K applies strictly only for methylammonium chromium alum but it also gives the order of magnitude of $g(T)$ for

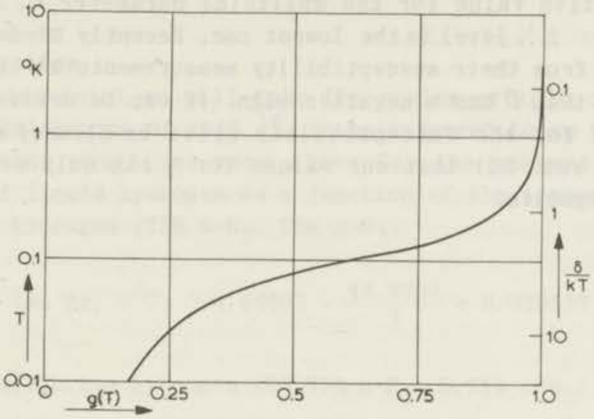

Fig. 35

$g(T)$ as a function of T for $\delta/k = 0.255^{\circ}$K.

potassium chromium alum. For both salts the influence of the exchange interactions is reduced by the crystalline field by a factor of 9/75 at temperatures which are small compared to δ/k. Finally, we will mention that the values of θ as mentioned above were recently confirmed by two other investigations.
Beun, Miedema and Steenland [89] found that the experimental relations between the susceptibilities of methylammonium chromium alum and potassium chromium alum and the temperature are in agreement with the calculated relations down to 0.3°K if extra θ's of - 0.01 and - 0.03°K respectively are introduced.
Bots [90] measured the fountain effect of liquid helium as a function of temperature down to 0.3°K using the susceptibility of potassium chromium alum as thermometric parameter. A small discrepancy between the experimental and theoretical values of the fountain effect disappeared when an extra θ of -0.03°K was used in the calibration of the magnetic thermometer.

5c. Manganese ammonium sulphate

Due to the fact that we did not determine the orientation of the crystalline axes with respect to the magnetic field the conclusions must be limited. Our values of Δ range from - 0.079 to + 0.032°K.

Bleaney and Ingram [82] considered the influence of the crystalline field and hyperfine splitting on the susceptibility of manganese ammonium sulphate. They also measured the paramagnetic resonance spectrum and the anisotropy of the susceptibility. They arrived at a positive value for the splitting parameter D. This means that the $S = \pm \frac{1}{2}$ level is the lowest one. Recently Miedema e.a. [91] concluded from their susceptibility measurements at temperatures below $1^{\circ}K$ that D has a negative sign. It can be derived from the equations for the susceptibility given by Bleaney and Ingram (eq. (10) ref. 82) that our values for Δ can only be explained if D is negative.

CHAPTER V

THE VAPOUR PRESSURE-TEMPERATURE RELATION OF LIQUID HYDROGEN

1. Introduction

As a starting point we will take the review article of Woolley Scott and Brickwedde of 1948 [10], to be referred to as WSB.
The following equations were given for the saturated vapour pressure of liquid hydrogen as a function of the temperature:
For normal hydrogen (75% $o\text{-}H_2$, 25% $p\text{-}H_2$)

$$\log p\ (\text{mm Hg, } 0^{o}\text{C}) = 4.66687 - \frac{44.9569}{T} + 0.020537\ T \qquad (1)$$

and for equilibrium hydrogen (99.79% $p\text{-}H_2$, 0.21% $o\text{-}H_2$)

$$\log p\ (\text{mm Hg, } 0^{o}\text{C}) = 4.64392 - \frac{44.3450}{T} + 0.02093\ T \qquad (2)$$

The equations were based on data obtained at the National Bureau of Standards in Washington. According to WSB they also represent the Leiden data on normal hydrogen within the limits of experimental accuracy. It follows from eqs. (1) and (2) that

$$\log p_{e\text{-}H_2}\ (\text{mm Hg, } 0^{o}\text{C}) - \log p_{n\text{-}H_2}\ (\text{mm Hg, } 0^{o}\text{C}) = -0.02295 + \frac{0.6119}{T} + 0.000393\ T \qquad (3)$$

The NBS measurements were based on the NBS scale. In 1939 several platinum resistance thermometers were calibrated at the NBS against a gas thermometer from the oxygen point down to 11°K. These calibrated thermometers defined the NBS scale. In later years other platinum thermometers were calibrated against the first ones, but up to now the NBS scale has been based on the calibrations of 1939.
In 1951 Hoge and Arnold [92] made new measurements of the saturated vapour pressure of equilibrium hydrogen up to the critical point. The temperature was measured with platinum thermometers using the NBS scale. The uncertainty in the NBS scale was estimated by Hoge and Arnold to be ± 20 m°K. The results were given in the form of a table of *pT* values. To avoid the trouble of interpolation

in a table Mr. F.H. Varekamp of the Kamerlingh Onnes Laboratory deduced an equation which represents the data in Hoge and Arnold's table very closely. The equation (for e-H_2) is

$$\log p(\mathrm{mm\,Hg},\ 0^{\circ}\mathrm{C}) = 4.63011 - \frac{44.2674}{T} + 0.021813\ T - 0.000021\ T^2 \quad (4)$$

Up to 25°K the differences between values from the table and those from the equation are less than 1 m°K. Near the critical point the differences become larger (see fig. 40).
Using eq. (3) giving the pressure differences between e-H_2 and n-H_2 determined by WSB one obtains for n-H_2 from (4)

$$\log p(\mathrm{mm\,Hg},\ 0^{\circ}\mathrm{C}) = 4.65306 - \frac{44.8793}{T} + 0.021420\ T - 0.000021\ T^2 \quad (5)$$

Eqs. (4) and (5) define the scale used in Chapter II and which is denoted by T_V.
The pT relation of n-H_2 was measured by Grilly [93] and by White, Friedman and Johnston [94] above the boiling point. Temperatures were measured with copper-constantan thermocouples. White e.a. deduced an equation which fitted their pT data within experimental accuracy and which at 20.4°K gave a d log p/dT in agreement with the WSB equation for n-H_2. Differences between the different pT relations for normal and equilibrium hydrogen and the T_V scale for e-H_2 (eq. (4)) are shown in fig. 40.
Several measurements of the boiling point of n-H_2 using a gas thermometer have been published. Van Dijk [77] recalculated the original data in a consistent way and found, averaging the data of five investigations made from 1931 up to 1954, 20.378°K for the boiling point of n-H_2. The boiling point of n-H_2 in the WSB scale (eq. (1)) is 20.390°K and 20.396°K in the T_V scale (eq. (5)). The boiling point of e-H_2 in the WSB scale is 20.273°K and 20.278°K in the T_V scale. For the calculation of the magnetic temperatures we used for e-H_2 as well as for n-H_2 at the boiling point $T_m - T_V = -18$ m°K. This means that in the magnetic scale the boiling point of n-H_2 is 20.378°K and the boiling point of e-H_2 is 20.260°K.

2. Results of measurements on manganese ammonium sulphate
The difference between the magnetic temperatures and T_V, obtained for n-H_2 are given in fig. 36. The final analysis was made after

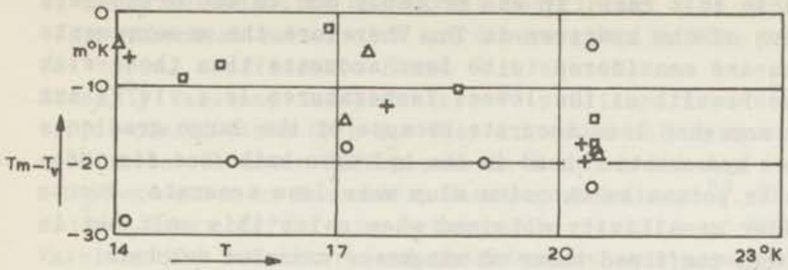

Fig. 36

Differences between magnetic temperatures T_m and vapour pressure temperatures T_V for normal hydrogen. T_V (n-H_2) is defined by eq. (5).

○ May 17 △ June 7
□ May 28 + Sept. 25

the definition of T_{58} for the helium region and the magnetic temperature used here is the one that fits T_{58}. In Chapter III it was called T_m'. The results for the series of December 18, 1958 with e-H_2 are given in fig. 37. In Chapter II it was

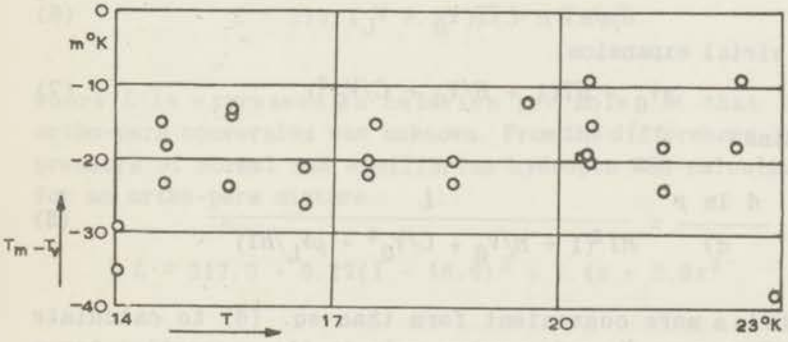

Fig. 37

Differences between magnetic temperatures T_m and vapour pressure temperatures T_V for equilibrium hydrogen. T_V (e-H_2) is defined by eq. (4).

mentioned that the measurements with n-H_2 were performed with hydrogen condensed only in the jacket, since it was not possible to make measurements with normal hydrogen in the thermometer reservoir (see section 3, Ch. II) because of the heating up which occurred in this case. It was probably due to the ortho-para conversion of the hydrogen in Th. Therefore, the measurements with n-H_2 are considered to be less accurate than those with e-H_2. The results at the lowest temperatures (e.g. 14°K) are probably somewhat less accurate because of the large gradients due to the hydrostatic head in the hydrogen bath (see fig. 46). The data on potassium chromium alum were less accurate, due to the smaller sensitivity obtained when using this salt, but in general they confirmed those on manganese ammonium sulphate. Assuming the boiling point of n-H_2 to be 20.378°K and that of e-H_2 to be 20.260°K our results point to a parallel displacement of the scale from 14°K to 23°K by 18 m°K. Taking into account uncertainties in the empty coil effect and in the vapour pressure measurement the uncertainty in the result of our measurements is such that the estimated maximum error in the temperature at 14°K is ± 15 m°K when the boiling point has been fixed.

3. Thermodynamic calculations

3a. Equations and quantities used

Using Clapeyron's equation

$$\mathrm{d}p/\mathrm{d}T = L/T(V_G - V_L) \tag{6}$$

and the virial expansion

$$pV_G = RT(1 + B/V_G + C/V_G{}^2) \tag{7}$$

one obtains

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{L}{RT^2(1 + B/V_G + C/V_G{}^2 - pV_L/RT)} \tag{8}$$

Eq. (8) is in a more convenient form than eq. (6) to calculate d ln $p/\mathrm{d}T$ because V_G and p enter only in the correction terms and p can therefore be taken from a provisional pT relation. The calculation requires the knowledge of L, the virial coefficients and V_L as functions of T.

1. The equation of state for gaseous normal hydrogen was given by WSB in the form

$$pV_G = RT(1 - \frac{A\rho}{T^{3/2}} - \frac{C\rho^2}{T^{3/2}}) \tag{9}$$

where ρ is the density of the gas and A and C are functions of

T. (C is not equal to the virial coefficient C in eqs. (7) and (8)). Numerical values of A and C were given by WSB. From these the virial coefficients B and C in eq. (7) can be evaluated. Recently Varekamp and Beenakker [95] published new data on the virial coefficients of n-H_2. They introduce only a second virial coefficient B. Later differences in B values between normal and e-H_2 were given by Beenakker, Varekamp and Knaap [96]. There is a rather large difference between the results of WSB and of Varekamp and Beenakker, and therefore we made separate calculations of the pT relation with both sets of data. Measurements on isotherms of n-H_2 from the boiling point to room temperature were made by Johnston and White in 1950. Only the final results were given [97]. From the pV/RT data at 20°K given in table 2 of ref. 92 we deduced a B value which is still lower than that given by WSB, but there seems to be some inconsistency in the data.
2. V_L data for normal and equilibrium hydrogen were given by WSB: The influence of the term pV_L/RT in eq. (8) is small.
3. The heat of vaporization of hydrogen was measured in 1923 by Simon and Lange [98] at several temperatures between the triple point and the boiling point. The results were given by the equation

$$L = 219.7 - 0.27\ (T - 16.6)^2 \qquad (10)$$

where L is expressed in calories per mole. At that time the ortho-para conversion was unknown. From the differences in vapour pressure of normal and equilibrium hydrogen WSB calculated that for an ortho-para mixture

$$L = 217.0 - 0.27(T - 16.6)^2 + 1.4x + 2.9x^2 \qquad (11)$$

in calories per mole, where x is the mole fraction of ortho hydrogen. In 1950 the heat of vaporization of equilibrium hydrogen at its boiling point was measured by Johnston, Clarke, Rifkin and Kerr [99]. They found 214.8 ± 0.4 cal/mole, whereas eq. (11) yields 213.4 cal/mole. The difference can be explained if the hydrogen used by Simon and Lange was converted into a mixture of 50% ortho and 50% para hydrogen. It may be mentioned that since L depends only slightly on T small changes in the temperature scales have a minor influence on L as a function of T.
Starting from Johnston's value of 214.8 cal/mole at the boiling

point of equilibrium hydrogen, L can be calculated at other temperatures using the equation*.

$$L_T = L_{T_0} + \frac{5}{2}R(T - T_0) - \int_{T_0}^{T} C_L \mathrm{d}T + \frac{RT}{V_G}\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right) - \left[\frac{RT}{V_G}\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right)\right]_{T=T_0} - \int_{p_0}^{p} V_L \mathrm{d}p \qquad (12)$$

C_L has been given as a function of T by Johnston e.a. [94], their data were in good agreement with those of Clusius and Hiller [100]. The other quantities entering into eq. (12) have been discussed above. The last four terms in eq. (12) are small, and the accuracy of them is probably such that no error beyond 1-2^o/oo in L_T is introduced by this calculation. The use of a provisional temperature scale in the measurement of C_L is also of minor influence.

3b. Calculations for e-H_2

A first calculation of d ln $p/\mathrm{d}T$ as a function of T was made using Johnston e.a.'s value of L at the boiling point, and Varekamp and Beenakker's data for B, and V_L from WSB applying eqs. (12) and (8). Numerical values of the quantities entering into eq. (12) are given in table VIII. 20.26^{o}K was chosen for the boiling point. $L_{20.26^oK}$ = 214.8 cal/mole = 898.74 J/mole (1 thermochemical calorie = 4.1833 int.joule = 4.1841 abs.joule) and R = 8.31662 J/mole ^{o}K. The calculations were made for 14, 16, 18, 20 and 21^{o}K. $\int_{20.26}^{T} C_L \, \mathrm{d}T$ was obtained by graphical integration of Johnston e.a.'s data. The data given by Varekamp and Beenakker [95] for B and $\mathrm{d}B/\mathrm{d}T$ for n-H_2 were used, and $B_{e\text{-}H_2} - B_{n\text{-}H_2}$ = 2 cm^3/mole and $(\mathrm{d}B/\mathrm{d}T)_{e\text{-}H_2} - (\mathrm{d}B/\mathrm{d}T)_{n\text{-}H_2}$ = -0.2 cm^3/mole ^{o}K taken from Beenakker, Varekamp and Knaap [96].
V_G was calculated from T, B and from p taken from the WSB scale for e-H_2 (eq. (2). For the calculation of $\int_{p_0}^{p} V_L \, \mathrm{d}p$ we used V_L = 27.5 cm^3/mole and p from eq. (2).
The values of L obtained are given in table VIII. (The last column gives the differences between the calculated values of L and L obtained from eq. (11)). Table IX gives the other quanti-

---

* Eq. (12) is analogous to eq. (9) Ch. III (see also ref. 8), the term with C can be neglected. The equation holds for monoatomic gases, but it can also be used for H_2 at low temperatures because practically all molecules are in their lowest rotational and vibrational states (see ref. 10).

TABLE VIII

Calculation of the heat of vaporization of e-H_2 as a function of T using $L_{20.26^{\circ}K}$ = 898.74 J/mole.								
T	$\frac{5}{2}R(T-20.26)$	$\int_{20.26}^{T} C_L dT$	B	$\frac{dB}{dT}$	$\frac{RT}{V_G}(B-T\frac{dB}{dT})$	$\int_{760}^{p} V_L dp$	L	ΔL
°K	J/mole	J/mole	cm^3/mole	cm^3/mole °K	J/mole	J/mole	J/mole	J/mole
14	- 130.16	- 102.51	-~~1~~253	24.8	- 4.79	- 2.55	909.01	+ 8.7
16	- 88.57	- 73.18	- 210	18.0	- 11.99	- 2.18	914.60	+ 7.1
18	- 46.99	- 41.42	- 179	13.5	- 21.60	- 1.45	913.18	+ 7.5
20	- 5.41	- 5.19	- 154	10.5	- 37.56	- 0.20	901.32	+ 6.4
21	+ 15.39	+ 15.61	- 144	9.3	- 47.97	+ 0.67	890.04	+ 4.0

TABLE IX

Calculation of d ln $p/\mathrm{d}T$ for e-H_2 using Varekamp and Beenakker's data for B. The last column gives d ln $p/\mathrm{d}T$ calculated with eq. (13).

T	$\dfrac{B}{V_G}$	$\dfrac{pV_L}{RT}$	$\dfrac{\mathrm{d}\ln p}{\mathrm{d}T}$	$\left(\dfrac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{eq.}(13)}$
$^\circ$K			$^\circ K^{-1}$	$^\circ K^{-1}$
14	- 0.0173	0.0018	0.5686	0.5685
16	- 0.0352	0.0044	0.4473	0.4475
18	- 0.0612	0.0088	0.3644	0.3644
20	- 0.0955	0.0155	0.3048	0.3047
21	- 0.1167	0.0197	0.2810	0.2810

ties used for the calculation of d ln $p/\mathrm{d}T$. In this step of the calculation we used the data given by WSB for V_L. The resulting values of d ln $p/\mathrm{d}T$ are given in the fifth column of table IX. It appeared to be possible to represent d ln $p/\mathrm{d}T$ within the limits of the accuracy of the calculation by the equation

$$\mathrm{d}\ln p/\mathrm{d}T = \frac{100.613}{T^2} + 0.05995 - 0.00034T \qquad (13)$$

(see table IX).
Eq. (13) yields on integration using p = 760 mm Hg at 0°C for $T = 20.26^\circ$K

$$\ln p(\text{mm Hg, } 0^\circ\text{C})^* = 10.45461 - \frac{100.613}{T} + 0.05995T - 0.00034T^2 \qquad (14)$$

Temperature differences between the scale defined by eq. (14) and the T_V scale for e-H_2 (eq. 4) are shown in fig. 38.
The calculation was repeated using B and C calculated from the WSB data for n-H_2. B and $\mathrm{d}B/\mathrm{d}T$ for e-H_2 were obtained by adding $B_{e\text{-}H_2} - B_{n\text{-}H_2} = 2$ cm^3/mole and $(\mathrm{d}B/\mathrm{d}T)_{e\text{-}H_2} - (\mathrm{d}B/\mathrm{d}T)_{n\text{-}H_2} = -0.2$ cm^3/mole $^\circ$K.

---

* Note that ln means logarithm to the base e, while log always denotes the logarithm to the base 10.

In the calculation of L from $L_{20.26}$, C and $\mathrm{d}C/\mathrm{d}T$ could be neglected. The terms in eq. (12) that were different from those in the foregoing calculation are listed in table X. It can be seen that the difference in L for the two calculations is insignificant. d ln $p/\mathrm{d}T$ was represented by:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{100.217}{T^2} + 0.06665 - 0.000730T \qquad (15)$$

Eq. (15) gives on integration using again $p = 760$ mm Hg at 0°C for $T = 20.26\,^\circ\mathrm{K}$

$$\ln p(\mathrm{mm\,Hg},\ 0^\circ\mathrm{C}) = 10.37937 - \frac{100.217}{T} + 0.06665T - 0.000730T^2 \qquad (16)$$

Differences in temperatures between this scale and the T_V scale (eq. (4)) have been plotted in fig. 38

TABLE X

Calculation of d ln $p/\mathrm{d}T$ for e-H_2 using the WSB data for B and C. The last column gives d ln $p/\mathrm{d}T$ as calculated with eq. (15).

T	L	B	C/V_G	$\frac{B}{V_G} + \frac{C}{V_G^2}$	$\frac{\mathrm{d}\ln p}{\mathrm{d}T}$	$\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{eq.(15)}}$
°K	J/mole	cm^3/mole	cm^3/mole		°K^{-1}	°K^{-1}
14	908.63	- 244	0.0	- 0.0167	0.5680	0.5678
16	914.32	- 202	0.7	- 0.0336	0.4465	0.4465
18	913.13	- 170	1.3	- 0.0575	0.3629	0.3628
20	900.92	- 147	2.0	- 0.0896	0.3026	0.3026
21	890.19	- 137	2.4	- 0.1083	0.2783	0.2786

It can be seen by comparing figs. 37 and 38 that there is a good agreement between the temperature defined by eq. (16) and the magnetic temperature as measured with manganese ammonium sulphate.

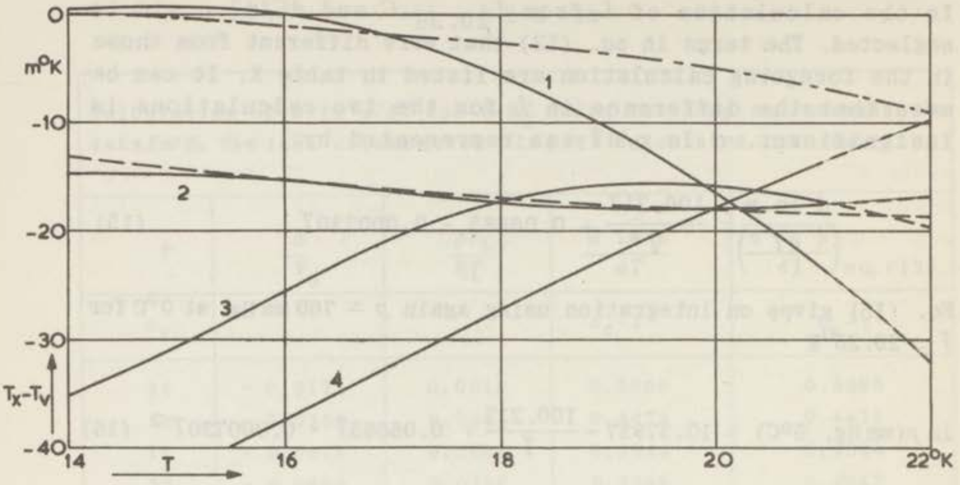

Fig. 38

Thermodynamically calculated pT relations for hydrogen compared with T_V.
1: $T - T_V$ (e-H_2), T is defined by eq. (14).
2: $T - T_V$ (e-H_2), T is defined by eq. (16).
3: $T - T_V$ (n-H_2), T is the scale calculated from L as given by Simon and Lange and B as given by Varekamp and Beenakker.
4: $T - T_V$ (n-H_2), T is the scale calculated from L as given by Simon and Lange and B as given by WSB.
– · – · T_{WSB} (eq. (2)) - T_V.
– – – – our proposed scale (see section 5).

3c. *Calculations for n-H_2*

The pT relation for n-H_2 was calculated using the heat of vaporization as given by Simon and Lange (eq. (10)). The calculations were made with the virial coefficients of WSB and with those of Varekamp and Beenakker. The calculations were performed in a somewhat less precise way. The pT relations were fitted to p = 760 mm Hg at 0°C for T = 20.38°K. The temperature differences between these pT relations and the T_V scale for n-H_2 as defined by eq. (5) have been plotted in fig. 38.

3d. *Discussion*

The differences at the boiling point of 18 m°K between the two pT relations calculated for e-H_2 and T_V(e-H_2) is trivial since we adopted 20.26°K for the boiling point whereas the T_V scale has a boiling point of 20.278°K. There is an appreciable difference between the *pT* relation calculated with the virial coefficients as given by Varekamp and Beenakker and the *pT* relation calculated with the virial coefficients as given by WSB. The latter is in very good agreement with our magnetic scale which pointed to a constant displacement of the Varekamp-Hoge-Arnold scale (eq. (4)) by 18 m°K when the boiling point was changed by 18 m°K. At low temperatures, where the influence of *B* is small, the slopes of both calculated scales are in agreement with the slope of the Varekamp-Hoge-Arnold scale and that of our magnetic scale. The difference at the boiling point of 16 m°K between the two *pT* relations calculated for n-H_2 and T_V (n-H_2) is a consequence of the choice of 20.38°K for the boiling point of n-H_2, whereas the T_V scale has 20.396°K. In this case the *pT* relation calculated with Varekamp and Beenakker's data for *B* is better in agreement with our magnetic scale than the *pT* relation calculated with the WSB data. At low temperatures there is no agreement between the slopes of the calculated *pT* relations and those of the magnetic and T_V scales.

We are inclined to give more weight to the two *pT* relations for e-H_2 since they are based on the later measurements of *L* by Johnston e.a. whereas in Simon and Lange's experiment the ortho-para concentration of the hydrogen was unknown. Moreover the *pT* relations calculated with Johnston e.a.'s data for *L* have the same slope as Hoge and Arnold's scale and our magnetic scale at the lower temperatures where the influence of the virial coefficients is small.

4. Recent tests of the NBS scale

Recently several laboratories calibrated platinum resistance thermometers with a gas thermometer down to 10 or 14°K, to investigate whether the international temperature scale above 90.19°K based on platinum resistance thermometers could be extended to lower temperatures. In some of these investigations a NBS Pt thermometer whose resistance was known in the NBS scale, was also measured.

In this way the NBS scale could be checked. Such measurements were recently carried out by Moessen and Aston at the Pensylvania State University and by Barber [102] at the National Physical Laboratory at Teddington. The results are shown in fig. 39 which is reproduced from Barber's paper [97*]. It can be seen that at

---

[*] We wish to thank Dr.C.R. Barber for providing us with a copy of this figure.

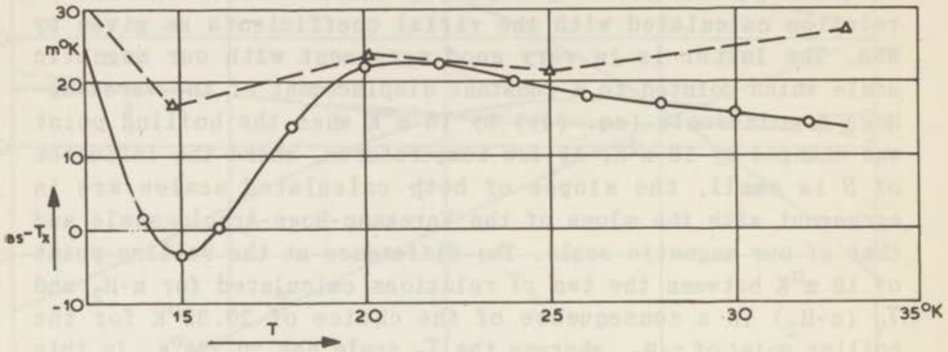

Fig. 39

Comparison of the NBS scale with recent data from NPL and PSU.
—○— T_X is temperature measured at NPL (Barber)
△ T_X is temperature measured at PSU (Moesson and Aston).

20°K there is agreement between the two investigations, both pointing to an error in the NBS scale of about 22 m°K. But at 15°K the NBS scale is 17 m°K too high according to Moessen and Aston whereas according to Barber it is 4 m°K too low.

It may be stressed that no hydrogen vapour pressures were measured in these investigations so that they can not give direct information on the *pT* relation of hydrogen. It is somewhat doubtful whether the data of WSB or of Hoge and Arnold can be adequately corrected for errors in the NBS scale because different platinum thermometers were used and no accuracy better than 0.02°K was claimed by the authors.

If we use the correction it confirms the conclusion drawn in section 1 from gas thermometer data that the boiling point of WSB and Hoge and Arnold is about 20 m°K too high. At 14°K no conclusion can be drawn because of the difference between Moessen and Aston and Barber's results.

One of the reasons that we did not extend our magnetic measurements on the *pT* relation of hydrogen was that our apparatus had been broken and the construction and calibration of new coils was necessary for which no time was available. By making more measurements with manganese ammonium sulphate and with iron ammonium alum and perhaps also with potassium chromium alum the uncertainty in our results could presumably be diminished.

5. Concluding remarks

The Advisory Committee on Thermometry in its session of 1958 stated that the best (rounded-off) value for the boiling point of normal hydrogen is 20.38°K.

There is, however, a tendency to use equilibrium hydrogen instead of normal hydrogen for accurate temperature measurements. In the two scales defined by eqs. (4) and (5) the difference between the boiling points of n-H_2 and e-H_2 is 0.118°K. Using this difference and 20.38°K for the boiling point of n-H_2 we find 20.262 for the boiling point of e-H_2.

In August 1959 an informal meeting* was held at the Kamerlingh Onnes Laboratory to discuss the temperature scale below the oxygen point. In this meeting it was considered advisable to take the rounded-off value 20.26°K for the boiling point of e-H_2. We wish to point out that if the boiling point in the scale of Hoge and Arnold (or Varekamp) had been adopted as a reference temperature the magnetic measurements would have been in agreement with this scale. Also thermodynamic calculations had given no reason for its replacement. But now it is desirable to shift the scale in such a way that it satisfies the boiling point of 20.26°K for e-H_2.

The way in which the scale is shifted remains to some extent arbitrary. In our opinion a reasonable way is to add to the scales defined by the Varekamp equations (4) and (5), the equation

$$\log p = 0.005274 - 0.000144T \qquad (17)$$

For e-H_2 this new scale can then be defined by the following equation obtained from eq. (4) by adding (17):

$$\log p(\text{mm Hg}, 0\,^{\circ}\text{C}) = 4.635384 - \frac{44.2674}{T} + 0.021669T - 0.000021T^2 \qquad (18)$$

This pT relation has for p = 760 mm Hg at 0°C, T = 20.2600°K and for the triple point pressure [10] p = 52.80 mm Hg at 0°C, T = 13.8000°K.

Accepting eq. (3) we obtain as the new scale for n-H_2:

$$\log p(\text{mm Hg}, 0\ \text{C}) = 4.658334 - \frac{44.8793}{T} + 0.021276T - 0.000021T^2 \qquad (19)$$

This equation gives for p = 760 mm Hg at 0°C, T = 20.3778°K.

---

* Attended by: C.R.Barber, F.G.Brickwedde, H.H. Plumb, H.F.Stimson, H. van Dijk, H. ter Harmsel, C. van Rijn, M. Durieux.

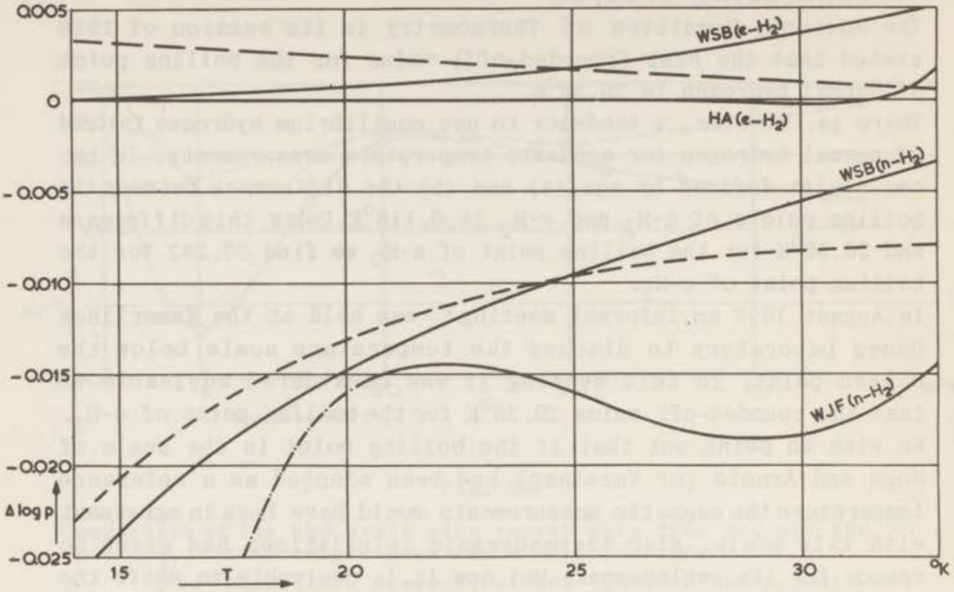

Fig. 40

Comparison of hydrogen vapour pressure temperature scales.
$p_V(e\text{-}H_2)$ is defined by eq. (4). $\Delta \log p = \log p_X - (\log p_V(e\text{-}H_2))$
WSB $(n\text{-}H_2)$: p_X defined by eq. (1)
WSB $(e\text{-}H_2)$: p_X defined by eq. (2)
WJF $(n\text{-}H_2)$: p_X defined by eq. (6) ref. 94
HA $(e\text{-}H_2)$: p_X defined from table 5 ref. 92
---- proposed scales for $e\text{-}H_2$ (eq. (18)) and for $n\text{-}H_2$ (eq. (19))

In fig. 40 differences in log p between several scales and the Varekamp-Hoge-Arnold scale for $e\text{-}H_2$ (eq. (4)) are given.
The temperature differences between the new scale and the T_V scale for $e\text{-}H_2$ below 22°K are shown in fig. 38.
The new scale for $e\text{-}H_2$ is within experimental accuracy in agreement with Hoge and Arnold's data over the whole temperature region (14 - 33°K). Below the boiling point the new scale for $n\text{-}H_2$ is in agreement with the NBS data within the accuracy of the NBS scale. Above the boiling point we can compare it with the data of Grilly [88] and of White, Johnston and Friedman [94]. For their measured points we refer to the original publications and ref. 92, fig. 3. It appears that Grilly's points, which are all below 24.5°K, are in agreement with our new scale, except for a constant change in the temperature of 0.02 - 0.03°K. The points

of White e.a. can be brought into agreement with our scale only from about 20 - 24^{o}K by a constant shift in the temperature of 0.02 - 0.03^{o}K, but at higher temperatures there is a larger difference. This could be improved by changing our scale for n-H_2 above 23^{o}K by about 0.05^{o}K at 30^{o}K but then the difference between the scales for n-H_2 and e-H_2 are no longer consistent with the differences as given by WSB (eq. (4)). We will not dwell on this subject because it is unlikely that the *pT* relation for n-H_2 will be used as a temperature scale above 24^{o}K.

Finally we may say that the scale for e-H_2 given by eq. (18) is within the limits of accuracy in agreement with most available data between 14 - 33^{o}K. The scale for n-H_2 (eq. (19) is in agreement with experimental data up to 23^{o}K. The accuracy in the scale for e-H_2 is probably ± 10 m^{o}K in the temperature and ± 3^{o}/oo in d*p*/d*T* from 14 up to 21^{o}K.

CHAPTER VI

VAPOUR PRESSURE THERMOMETERS. TEMPERATURE GRADIENTS IN LIQUID HELIUM.

1. Introduction

The vapour pressure scale for liquid helium being fixed to about $\pm 2\,m^{o}K$, it is important to investigate how accurately temperature measurements from the vapour pressure can be made. In experiments in which it is unnecessary to know the temperature very accurately the vapour pressure is generally measured at the top of the cryostat filled with liquid helium. When there are vapour bubbles throughout the liquid helium bath, and they are at every height in thermal equilibrium with the liquid, a temperature gradient in the helium bath can be expected corresponding to the hydrostatic pressure gradient (see fig. 41). Below the λ-point the liquid evaporates only at the surface, and the high heat conductivity keeps the temperature uniform throughout the liquid. However, the results from Chapter II and also other experiments indicate that the actual temperature gradient in a helium bath above the λ-point is not always equal to that derived from the hydrostatic pressure head. The use of a separate

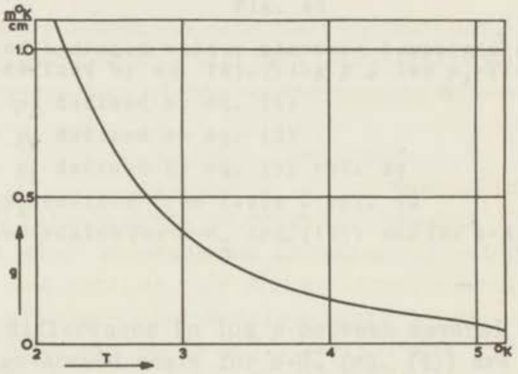

Fig. 41

Temperature gradient g in liquid helium corresponding to the hydrostatic pressure head.

vapour pressure thermometer is desirable for accurate temperature measurements. Vapour pressure thermometers have been used by many investigators. The glass vapour pressure thermometer described in Chapter II proved to be satisfactory for measurements of temperatures within the bulb. For measurements of the temperature of the bulk helium or of an object outside the bulb a copper bulb is more appropriate. We made a glass and a metal vapour pressure thermometer, placed them next to each other in a dewar, and compared the pressures in both thermometers with each other and with the bath pressure [103]. As we were also interested in the reproducibility of resistance thermometers of several kinds, seven resistance thermometers were placed in the bath near the vapour pressure thermometer bulbs, and measurements of the resistances were made. Recently the study of temperature gradients in a liquid helium dewar has received some interest, at first only because of practical reasons of thermometry but afterwards, when some interesting features had been found, also for the phenomenon itself. Three different investigations have been made [104,105,106]; for two of them only preliminary data have been published.

In this chapter we will first describe our experimental set-up and the results obtained. After this a summary is given of the three other investigations. Finally, a discussion of possible errors in vapour pressure measurements and some concluding remarks are made.

2. Experimental method

The glass vapour pressure thermometer was of similar construction to the one used for the magnetic measurements. Only in this case the outer tubes carrying the coils were omitted and the thermometer reservoir was a simple closed bulb (see fig. 42a). The inner side of the jacket J was silvered and the bulb was painted white to combat radiation. The dimensions of the tubes C and E and of the constriction Q were the same as described in Chapter II.

The metal vapour pressure thermometer is shown in fig. 42b. The copper bulb Th was connected to the manometer by the stainless steel capillary C_1. The lowest part of C_1 ($\approx$ 30 cm) had an inner diameter of 1.5 mm and an outer diameter of 2.0 mm. The size of the higher part of C_1 was 2.0 mm i.d. and 2.5 mm o.d. (The wall of C_1 has been drawn in fig. 42b as a single line). The german silver outer tube C_2 had an inner diameter of 4 mm and an outer diameter of 5 mm. C_1 and C_2 were hard-soldered to each other at their lower sides with a copper spacer between them. The two

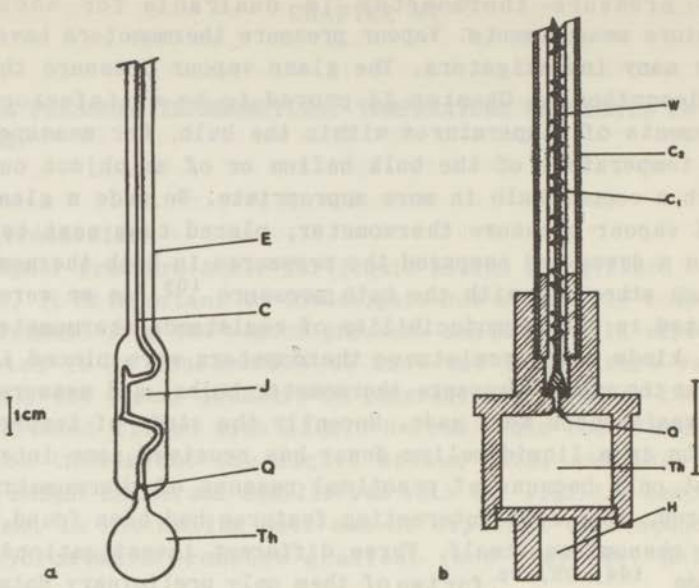

Fig. 42

a. The glass vapour pressure thermometer.
b. The metal vapour pressure thermometer.

tubes were soft-soldered to the bulb Th. The bottom of Th was also soft-soldered. The space H in the bottom served for the mounting of a germanium resistance thermometer in a platinum capsule. A constantan wire W on which small pieces of wire were twisted was placed in the inner capillary C_1 to avoid oscillations in the gas and to prevent high temperature radiation from entering into Th. The wire rested on the edge of the opening Q. The diameter of Q was kept small (0.5 mm) to diminish the film creep. The tube C_2 surrounded the inner one over its whole length in the dewar. Outside the cryostat the tubes C_1 and C_2 were connected to each other via a bellows to prevent tension from occurring in the tubes when the dewar was cooled while the jacket had been evacuated.

The glass and the metal vapour pressure thermometer, were placed next to each other with their reservoirs in holes in a copper cylinder 2 cm high and 4 cm in diameter. The copper bulb fitted tightly into the copper cylinder, the glass bulb more loosely. The copper block was suspended from the outer tube C_2 of the metal vapour pressure thermometer by three constantan wires about

3 cm long. The lower side of the block was about 3 cm above the bottom of the dewar. On the bottom of the dewar lay a heating element as described in Chapter II. Its resistance was 56Ω. The dimensions of the dewar are given in Chapter II.

Two more holes were made in the copper block, in which two phosphor-bronze resistance thermometers were placed. Four carbon thermometers were mounted under the copper cylinder. They had no metal contact with the cylinder. A germanium thermometer in a platinum capsule * was placed in the hole H below the metal vapour pressure thermometer.

Measurements of vapour pressures and resistances were made in the liquid helium and hydrogen regions. The absolute pressure was measured with mercury manometers. Differences between the pressures in the thermometer reservoirs, p_{Th}, in the jackets, p_{J}, and the pressure over the bath, p_{B}, were measured with a double oil manometer. p_{B} is the pressure measured at the cap of the cryostat just above the glass dewar. About 0.5 cm^3 of liquid was condensed in the thermometer vessels Th. There was either a small amount of liquid or exchange gas in the jackets, or they were evacuated. Results of measurements of differences between p_{Th}, p_{J} and p_{B} will be given both for the glass and the metal vapour pressure thermometer and for temperatures between 5.2 and 1.3°K. Some results of the resistance measurements near the λ-point will also be mentioned.

3. Results and discussion

3a. Results at 4.2, 3.2 and 2.2°K

The results obtained at 4.2, 3.2 and 2.2°K on several days are shown in fig. 43. Measured pressure differences $p_{\mathrm{Th}} - p_{\mathrm{B}}$ and $p_{\mathrm{J}} - p_{\mathrm{B}}$ both for the glass and metal vapour pressure thermometer were converted into temperature differences using $\mathrm{d}p/\mathrm{d}T$ as given in ref. 33. A correction for the aerostatic pressure head in the tubes C, E, C_1 and C_2 (fig. 42) was applied. The correction was only applied for the parts of the tubes immersed in the liquid, assuming that the gas in this part had the saturated density at the bath temperature. When the jackets were evacuated only 50% of this correction was used because in this case the average temperature of the gas in C and C_1 was higher than the bath temperature. The correction was small (see fig. 5). In fig. 43 it is indicated whether there was some liquid in the

---

* The germanium thermometer was made by the Bell Telephone Laboratory and kindly placed at our disposal by Prof. H.A. Boorse, Columbia University, New York.

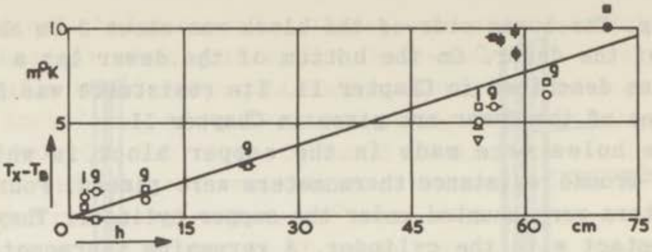

Fig.43a

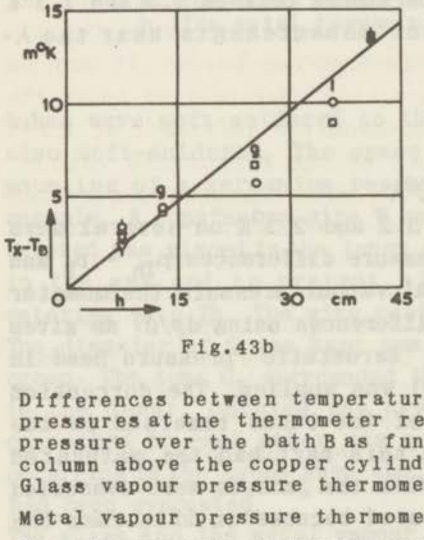

Fig.43b

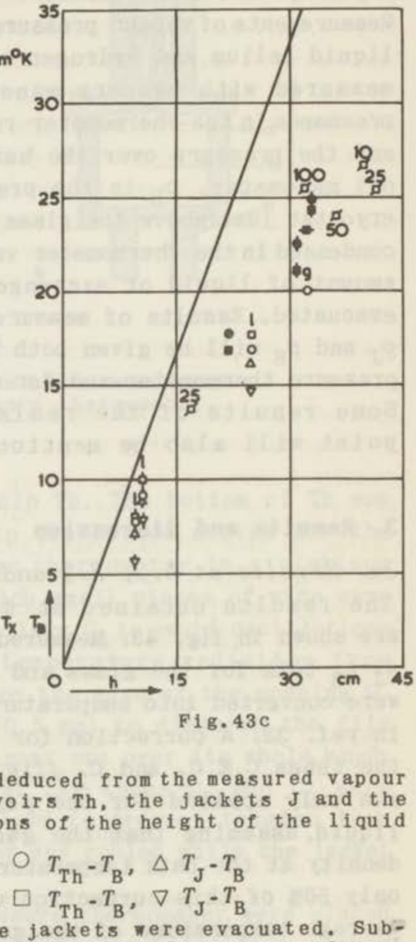

Fig.43c

Differences between temperatures deduced from the measured vapour pressures at the thermometer reservoirs Th, the jackets J and the pressure over the bath B as functions of the height of the liquid column above the copper cylinder.

Glass vapour pressure thermometer: ○ $T_{Th}-T_B$, △ T_J-T_B

Metal vapour pressure thermometer: □ $T_{Th}-T_B$, ▽ T_J-T_B

The black points indicate that the jackets were evacuated. Subscripts l and g denote whether there was some liquid or only gas in the jackets. Results obtained on different days have been indicated as ○ Oct.23. ⌽ Nov.4, -○-Nov.13, ⌀ Feb.20. The heating current (through 56Ω) has been indicated for the points of Feb. 20.

The solid lines give the calculated hydrostatic head correction.

a. 4.2°K, b. 3.2°K, c. 2.2°K

jackets or whether they were gas-filled or evacuated. The straight lines indicate the theoretical hydrostatic pressure head effect calculated from the liquid column above the upper side of the copper cylinder, using the ratio between the density of liquid helium and mercury and dp/dT as given in ref. 33. On Oct. 23 the jackets were evacuated at 4.2°K to a pressure less than 10^{-5} mm Hg, on the other days at 77°K. On the first three days the heating power was in most cases 35 mW, sometimes 20 or 70 mW. On Feb. 20 the dependence of the pressure in the metal vapour pressure thermometer on the heater current was investigated. The heater current in mA is indicated in the figure.

The results may be summarized as follows: The temperatures in the metal and glass vapour pressure thermometer reservoirs were equal to within about 1 m°K. These temperatures were independent of whether the jackets were gas-filled or whether there was some liquid in the jackets. If the hydrostatic pressure head correction did not exceed 5 m°K, the temperatures measured with the vapour pressure thermometers were equal to the temperatures deduced from the pressure over the bath by adding the hydrostatic head correction. If the hydrostatic pressure heads were larger, the temperature measured with the vapour pressure thermometers was always lower than that calculated from the bath pressure and the hydrostatic head. The pressures in the vapour pressure thermometers did not depend much on the heating power. It may be remarked that after switching over to a higher heating power, the pressure in the vapour pressure thermometer decreased at first owing to the cooling of the tubes by the evaporated vapour. The pressures in the jackets were always somewhat lower than those in the thermometer reservoirs, especially in the case of the metal vapour pressure thermometer (see fig. 43). This was probably due to a condensation effect (see section 5). When the jackets were evacuated, the pressures in both vapour pressure thermometers were the equivalent of 2-4 m°K higher than in the case when the jackets were gas-filled. The time required to reach equilibrium was measured in the case when the jackets were gas-filled. When the temperature in the dewar had been raised, the temperature in the glass vapour pressure thermometer, as measured from its pressure, increased and tended to equilibrium with a time constant of about 6 minutes. When the temperature in the dewar had been decreased, the time constant of the glass vapour pressure thermometer for reaching its equilibrium was about 2 minutes. Both measurements were made at 4.2°K at a heating power of 30 mW. The metal vapour pressure thermometer reached equilibrium much faster.

3b. Measurements below the λ-point

Above 1.5°K the pressure in the metal vapour pressure thermometer was equal to the bath pressure within the equivalent of 1 m°K, whether the jacket was gas-filled or evacuated (see fig. 44).

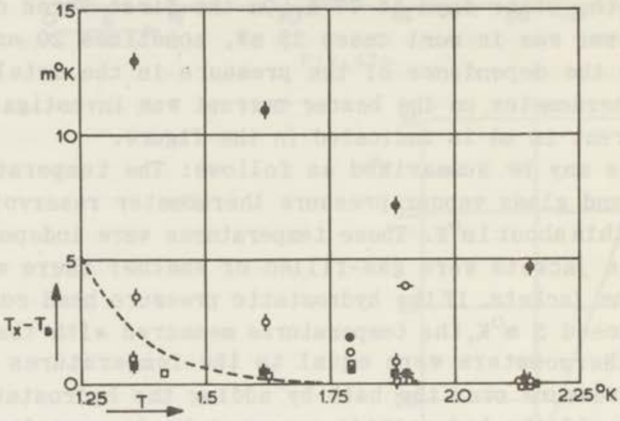

Fig. 44

Differences between temperatures deduced from measured vapour pressures at the thermometer reservoirs, the jackets and the bath below the λ-point. Points have been marked as described under fig. 43. The broken line indicates the correction for the thermomolecular pressure effect in a tube of 2 mm i.d.

For the glass vapour pressure thermometer this was only the case above 1.8°K, when the jacket was gas-filled (the point at 1.9°K, $T_{\mathrm{Th}} - T_{\mathrm{B}}$ = 3.9 m°K, is probably an experimental error). At lower temperatures the pressure in the glass vapour pressure thermometer was higher than the bath pressure, even when the jacket was gas-filled. When the jacket was evacuated, rather large differences between the pressure in the glass vapour pressure thermometer and the bath pressure occurred even just below the λ-point. On Nov. 4, when the jacket was evacuated at 77°K, the differences were larger than on Oct. 23 when the jacket was evacuated at 4.2°K. The warming up was probably mainly caused by the heat input due to the film creep. Below 1.45°K the thermomolecular pressure effect becomes of importance.

3c. Results obtained on November 13

Measurements were made at 16 temperatures between 5.0 and 1.8°K.

The jacket of the metal vapour pressure thermometer was evacuated during the first 6 series. Then it was filled with gas. The jacket of the glass vapour pressure thermometer was filled with gas all the time. The results at all temperatures above the λ-point show a behaviour similar to that given in fig. 43 for 4.2, 3.2 and 2.2°K (see fig. 45). The sequence of the series is indicated in the figure by numbers. When the liquid level was very low, the temperature of the glass vapour pressure thermometer rose somewhat above that of the metal vapour pressure thermometer, evidently due to the heat leak from above.

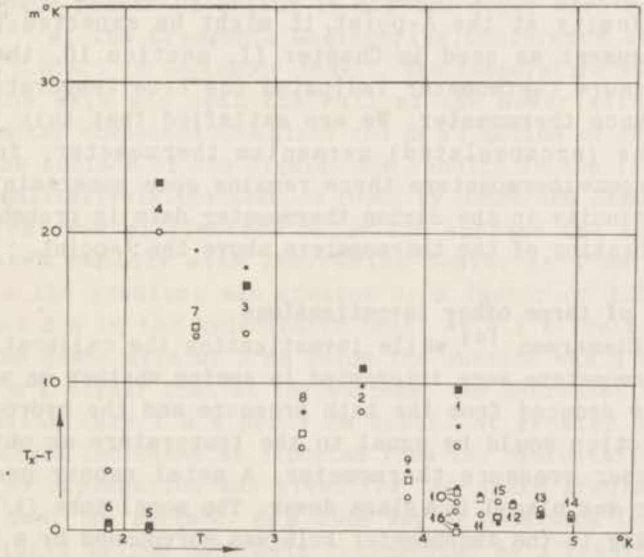

Fig. 45

Differences between temperatures deduced from the vapour pressure measured at the thermometer reservoir, at the jacket and over the bath as functions of the temperature.

○ $T_{Th} - T_B$ for the glass vapour pressure thermometer.

□ $T_{Th} - T_B$ for the metal vapour pressure thermometer.

■ $T_{Th} - T_B$ for the metal vapour pressure thermometer with vacuum jacket.

The small black circles indicate the calculated hydrostatic head effect.

3d. Results of the resistance versus vapour pressure data near the λ-point

The thermometer calibrations were made by Mr. C. van Rijn. Empirical equations were fitted to the data, and differences were plotted between temperatures deduced from these equations and T_{58} deduced from the vapour pressures in the metal vapour pressure thermometer with gas-filled jacket. Van Rijn found, near the λ-point, the following behaviour of these deviation curves:

PhBr I: no noticeable discontinuity; PhBr II a discontinuity between 2 and 4 m^{o}K; Carbon resistor 1: a discontinuity of 2-4 m^{o}K; Carbon resistor 3: a discontinuity of 2-10 m^{o}K; Germanium resistor: a discontinuity smaller than 1 m^{o}K. When there was a discontinuity, the temperature derived from the resistance was always too high, above the λ-point. When there was no discontinuity at the λ-point, it might be expected from a similar argument as used in Chapter II, section 10, that the vapour pressure thermometer indicated the true temperature of the resistance thermometer. We are satisfied that this is the case for the (encapsulated) germanium thermometer; for the phosphor-bronze thermometers there remains some uncertainty and the discontinuity in the carbon thermometer data is probably due to a superheating of the thermometers above the λ-point.

4. Summary of three other investigations

Hoare and Zimmerman [104], while investigating the calibration of carbon thermometers, were interested in seeing whether or not the temperature deduced from the bath pressure and the hydrostatic head correction would be equal to the temperature as obtained with a vapour pressure thermometer. A metal vapour pressure thermometer was placed in a glass dewar. The monel tube (1/8 inch o.d.) leading to the thermometer bulb was surrounded by a vacuum jacket. The vapour pressure thermometer could be moved up and down by means of a sliding O-ring. To decrease the heat input along the inner tube leading to the bulb, a copper wire was soldered between the inner and outer tubes of the vacuum jacket to serve as a thermal shunt. An attempt to provide for thermal contact between the inner tube and the bath by means of transfer gas in the jacket led to oscillations of the gas in the inner tube. The measurements of the pressure as a function of the immersion depth showed a remarkable feature near the surface of the liquid. When the vapour pressure thermometer was immersed in the liquid half way to the vertical walls of the bulb, its pressure was only the equivalent of one or two millidegrees higher than the bath pressure, but at an immersion depth of 1 cm the differences were 3 and 8 millidegrees at 3.4 and 2.5$^{\text{o}}$K respectively. At increasing immersion depth the temperature measured with the vapour pressure thermometer was always higher than deduced from the bath pressure and the hydrostatic head correction. Hoare and Zimmerman observe: "The observations are readily explained if there is a surface layer on a pumped helium bath through which a sharp temperature gradient exists. Whatever the cause of this, the effect manifests itself by some degree of superheat in the liquid. The degree of superheat is diminished by increasing the power input at the bottom of the dewar and hence the bubble evolution rate, but it does not appear possible to eliminate the effect merely by increasing the power input".

Measurements concerning the temperature distribution in the liquid and vapour phases of helium in a glass dewar were reported by Swim [106] at the Cryogenic Engineering Conference at Berkeley (Cal., U.S.A.) in September 1959 *. The temperature was measured near the axis and near the wall of the dewar with a carbon thermometer connected to a glass rod as a function of the distance from the surface of the liquid. The results in the liquid phase were qualitatively the same as found by Hoare and Zimmerman. For the first few millimeters below the surface the temperature increased rapidly with increasing depth. At 1 mm below the surface the gradient was greater by a factor of 126 than the gradient due to the hydrostatic head. At 4.1$^{\text{o}}$K the temperature near the dewar axis at 2 mm below the surface was 3 m$^{\text{o}}$K and at 4 mm 5 m$^{\text{o}}$K higher than at the surface, the hydrostatic pressure head being only 1 m$^{\text{o}}$K per 7 cm depth. At greater depths the temperature increased as expected from the hydrostatic pressure head. No explanation was given for the sharp gradient in the liquid near the surface. As a crude way of obtaining temperatures in a liquid helium bath, Swim recommended as a result of these measurements that 5 m$^{\text{o}}$K simply be added to the temperature deduced from the pressure over the bath after correction for the hydrostatic head.

Plumb investigated the temperature distribution in a glass dewar and found it irreproducible [13]. Later on he used a liquid helium storage vessel with a copper inner wall filled with about 10 liters of liquid helium. Measurements were made with carbon thermometers and a vapour pressure thermometer. Preliminary results were reported in Copenhagen, August 1959 [105]. Plumb's

---

* We would like to thank Dr. R.T. Swim (Naval Research Lab., Washington) for sending us a copy of his paper presented at this Conference.

conclusion was that in such a storage vessel no temperature gradients exist larger than a fraction of a millidegree. We will give here the figures on his vapour pressure thermometer because they give information about the heat leak down the tube leading to the thermometer bulb. With a vacuum shield around this tube ending about 3 cm above the copper vapour pressure bulb, the temperature in the vapour pressure thermometer was 2.5 $m^{O}K$ higher than the temperature at the surface of the bath. Without a vacuum shield, the temperature of the vapour pressure thermometer was only 0.6 $m^{O}K$ higher than the surface temperature. Finally a radiation shield was introduced; the resulting temperature difference was 0.1 $m^{O}K$. All figures were to a high degree independent of the immersion depth, showing that no gradient due to the hydrostatic head existed.

5. Discussion

The results of the four investigations can be summarized as follows:

1. Using a vapour pressure thermometer with gas-filled jacket, either of glass or metal construction, temperatures were found by us in a glass dewar corresponding to the hydrostatic pressure head in the liquid for hydrostatic heads up to 5 $m^{O}K$. At higher hydrostatic heads the temperature was always lower than calculated from the hydrostatic pressure head. With an evacuated jacket the measured temperatures were 2-4 $m^{O}K$ higher than with a gas-filled jacket.
2. Using a vapour pressure thermometer with vacuum jacket and thermal shunt, Hoare and Zimmerman found temperatures in liquid helium in a glass dewar 3-5 $m^{O}K$ higher than calculated from the hydrostatic pressure head, with a heat input of 200 mW at the bottom of the dewar. A sharp temperature gradient was observed just below the surface.
3. Using a carbon thermometer Swim found a temperature rise of 5 $m^{O}K$ just below the surface of the liquid in a glass dewar, and at greater depths of immersion, a temperature gradient corresponding to the hydrostatic head.
4. Plumb found no temperature gradient exceeding 0.1 $m^{O}K$ in liquid helium in a copper storage vessel.

The results of Plumb show that the temperature distribution in liquid helium in a copper storage vessel is distinctly different from that in glass dewars. In the copper wall no appreciable temperature differences can occur, and as long as no heat is introduced in the liquid, in equilibrium conditions this has everywhere the temperature of the copper wall.

The gradients found in glass dewars by Hoare and Zimmerman and by Swim differ from our results. In view of this difference we shall discuss possible errors in temperature measurements with a vapour pressure thermometer starting from the following remarks given in 1955 at a meeting on the liquid helium temperature scale * in Leiden [49]:

a. Cold spots should be avoided.
b. Heat influx to the vapour pressure bulb from above must be avoided.
c. Oscillations must be avoided.
d. Temperature gradients in the bulb should be avoided.

The effect of cold spots. Suppose a single walled tube connects the vapour pressure bulb to the manometers. When a gradient due to the hydrostatic head exists in the bath, this tube passes through liquid that has a lower temperature than the liquid at the depth of the bulb. When the heat introduced from above is not sufficient to keep the temperature of the inner wall of the tube above, or at least equal to, the temperature of the helium in the bulb, the vapour can condense on the wall at "cold spots". In consequence there will be an upward gas flow in the tube and liquid will flow down into the bulb. The temperature of the liquid in the bulb will decrease due to the evaporation of liquid and there will be a heat flow from the bulk helium to the bulb. In the tube where condensation takes place there will be a heat flow from the inner wall of the tube to the bath.

The process affects the temperature measurements in two ways: First, the pressure measured with the manometer will be lower than the pressure in the bulb due to the pressure drop in the tube. Second, the temperature in the bulb will be lower than that in the surrounding bulk helium.

To avoid the condensation effect a jacket around the tube leading to the vapour pressure bulb is often used. In the case when this jacket is evacuated, the occurrence of cold spots and condensation is impossible, but a fairly large amount of heat flows down the central tube into the bulb. In the case when gas is in the jacket condensation could still occur. Only approximate calculations of the condensation effect can be made.

The influence of the condensation effect on the measured temperature can be estimated as follows: Suppose

---

* Attended by: E. Ambler, J.R. Clement, H. van Dijk, R.P. Hudson, W.E. Keller, D. de Klerk and M. Durieux.

the height of the liquid column above the thermometer reservoir to be h and that there be a uniform temperature gradient g in the bath, the temperature being the lower at higher level. Let us assume the pressure drop to be of second order importance so that the pressure in the inner tube has everywhere the value corresponding to the temperature of the helium in the thermometer reservoir Th. Under this assumption, if no heat is introduced from above, the temperature at the inner wall of the central tube is everywhere equal to T_{Th} due to the condensation. Assuming that the temperature of the bulk helium just outside the reservoir of the vapour pressure thermometer equals T_{Th}, the total amount of heat that flows per second from the inner tube to the bath equals

$$\dot{Q} = \tfrac{1}{2} g h^2 / R \tag{1}$$

where R is the heat resistance per cm of height between the inner wall of the inner tube and the bulk helium. In case the pressure drop is not negligible, or the condensation decreases the temperature in Th below that of the bulk helium outside Th, the heat flow will always be smaller than given in eq. (1).

For a single-walled stainless steel tube of 2 mm i.d. and 3 mm o.d., $1/R \approx 34$ mW/cm °K [107], so that when $g \approx 1$ m°K/cm and $h = 20$ cm, $\dot{Q} = 7$ mW. For a glass or stainless steel tube 2 mm i.d. and 3 mm o.d., surrounded by a gas-filled jacket and an outer tube of 5 mm i.d. and 6 mm o.d., the heat resistance is practically equal to the heat resistance of the gas-filled jacket, in this case $1/R \approx 0.7$ mW/cm °K. If $g = 1$ m°K/cm and $h = 20$ cm, $\dot{Q} = 0.14$ mW. Possible heat resistances of boundary layers, but also a decrease of the heat resistance of the gas in the jacket due to convection have been neglected. The amount of liquid that evaporates and the pressure drop can be calculated. It follows that the pressure drop in the central tube is negligible even in the case of the single walled stainless steel tube.

The temperature difference between the liquid in the reservoir and the bulk helium due to the heat flow $\dot{Q}$ depends on the heat resistance between the two liquids. In the case of a glass bulb with a surface area of 6 cm^2 and a wall thickness of 1 mm, a heat flow of 0.14 mW needs a temperature gradient over the glass of about 3 m°K and less than 0.1 m°K in the case of a copper bulb, when only the heat resistance of the wall is taken into account. A possible temperature difference between the bulk helium and the copper or glass wall when there is a flow of heat depends probably on the flow of the liquid around the wall and on the position of the wall and is not easy to calculate. Our metal vapour pressure thermometer had a total outside surface area (without the copper cylinder) of 18 cm^2. In the case of the gas-filled jacket the calculated heat flow per cm^2 is less than 0.01 mW. It is not likely that this gives a temperature difference larger than 1 m°K between the bulk helium and the copper wall. The calculation was carried out for $g = 1$ m°K/cm, which holds for $T = 2.2$ °K. At 4.2 °K $g = 1$ m°K/7 cm and all figures are a factor of 7 smaller.

The result of the approximate calculations is that the difference between the temperature measured with the metal vapour pressure thermometer with gas-filled jacket and the temperature of the bulk helium just outside the thermometer bulb due to a condensation effect is smaller than 1 m°K even in the case of a helium height of 20 cm at 2.2°K. For the glass vapour pressure thermometer with gas-filled jacket an effect of a few millidegrees just above the λ-point cannot be excluded from the calculation alone.

It has been shown in Chapter II that the temperature deduced from the measured vapour pressure was equal to the temperature of the paramagnetic salt to within ± 1 m°K. This proves that, indeed, the pressure drop due to a possible condensation at cold spots was small in the glass apparatus.

Condensation, if present, had a greater effect in the jacket than in the inner tube, both for the glass and the metal vapour pressure thermometer. Therefore, it can be expected that the temperature differences between the jackets and the bulk helium (just outside the jacket) were larger than the temperature differences between the thermometer bulbs and the bulk helium. The small temperature differences measured between the jackets and the thermometer bulbs are a strong indication that the temperature difference between the thermometer bulb and the helium in the bath at the same height was also small.

Heat influx into the vapour pressure thermometer. When an evacuated jacket is used there will be a heat influx through conduction along the wall of the inner tube and by the gas in this tube and through radiation. The heat influx along a stainless steel capillary of 2 mm i.d. 2.5 mm o.d. and 1 m length when one end is at 300°K and the other at liquid helium temperature is about 6 mW [107]. For a glass tube of 2 mm i.d. and 3 mm o.d. under the same conditions the heat influx is 0.8 mW. It is difficult to estimate the radiation that reaches the thermometer bulb through the inner and outer tubes because an unknown part is absorbed at the walls.

The temperature rise of both our vapour pressure thermometers when the jackets were evacuated was about 3 m°K. In the case of the glass vapour pressure thermometer the heat must be conducted through the glass wall (near Q, see fig. 42a) that is in contact with the bath. In the case of the metal vapour pressure thermometer the heat coming from above is distributed over the whole wall of the thermometer vessel, because no significant temperature differences can occur in the copper. Perhaps the heat is also distributed over the cylinder which fits closely around the bulb. The temperature rise of 3 m°K is then due to a difference between the temperatures of the copper and of the bulk helium.

When the heat transfer from the copper bulb to the bulk liquid is the critical step, the radiation that reaches the bulb from

the outside can also effect its temperature. It may be expected that this effect is more important for the flat reservoir of the vapour pressure thermometer used by Hoare and Zimmerman especially when the reservoir comes near the liquid surface. Quantitative data on heat transfer between an aluminium plate and liquid helium at comparatively large heat flow have been published by Grassmann e.a. [108]. At a heat current density of 20 mW per cm^2, temperature differences are given of 0.07, 0.15 and 0.23°K at 3.57, 3.05 and 2.83°K respectively. It would be interesting to obtain quantitative data about the heat influx to the reservoir of a vapour pressure thermometer and to measure the rise in temperature of the vapour pressure thermometer when a measured small amount of heat is applied to the bulb.
In this connection it may be remarked that the heat-flow to the surface of the carbon thermometer used by Swim due to the radiation can possibly be larger than the heat developed in the thermometer by the measuring current. We do not wish to suggest that a heating up due to radiation is the reason that the results found both by Hoare and Zimmerman and by Swim are different from ours, but it cannot be excluded that it might affect their results in some way.

Oscillations. As mentioned oscillations in the gas in the central tube occurred in the vapour pressure thermometer of Hoare and Zimmerman when there was exchange gas in the jackets. In our vapour pressure thermometers we could never detect any oscillations. Information about the effect can be found in ref. 109.

It is not likely that significant temperature gradients occurred in the liquid in the vapour pressure thermometers used by Hoare and Zimmerman or by us.

6. Concluding remarks

The temperature distribution in liquid helium in a glass dewar is more complicated than expected. It is not always that which is calculated from the hydrostatic head effect. It seems to be dependent on the particular type of dewar or apparatus in the dewar in a way which is not sufficiently well understood.
For the gradient as found by us the following qualitative argument can be given: The heat influx by the heater tends to raise the temperature in the liquid up to that expected from the hydrostatic head when no superheating occurs. The convection and conduction in the liquid tend to equalize the temperature. This leads to a compromise. It seems reasonable to suppose that in

the vapour bubbles the temperature has at least the value calculated from the hydrostatic pressure *. This seems to be in contradiction to a temperature of the helium in the dewar that is lower than expected from the hydrostatic pressure, but when the heating power is 30 mW, less than 1% of the volume of the liquid is occupied by bubbles.

A temperature distribution as found by Hoare and Zimmerman and by Swim can be understood, as stated by Swim, if there is a strong absorption of heat just below the surface and some superheating at greater depth. In this case the temperature at the surface of the bubbles is probably lower than in the liquid.

For accurate measurements it is advisable to use a vapour pressure thermometer, and in general a copper bulb is preferred. Even then, the bulb may rise in temperature when too much heat comes from above. Our experience with a gas-filled jacket was quite satisfactory but it can give rise to oscillations in the central tube when no precautions are taken. In the liquid, temperature fluctuations of several millidegrees occur [106]. Whenever very accurate temperature measurements are necessary, the object whose temperature is desired to be known can better be separated from the bulk helium and placed in a copper box in which the reservoir of the vapour pressure thermometer is incorporated. Below the λ-point a metal vapour pressure thermometer with copper reservoir and a capillary of inner diameter of 2 mm can be used down to 1.4°K, though the temperature deduced from the pressure over the bath is as good. Below 1.4°K the thermomolecular pressure effect becomes important and temperatures can better be determined from the bath pressure. At very low temperatures, e.g. below 1°K, the pressure drop in the gas over the bath has to be taken into account, when the evaporation rate is not small. The use of a pressure tube ending at a small height above the liquid removes this uncertainty, but to reach a temperature accuracy of 1 m°K at 1°K this tube has to have a diameter of at least 28 mm because of the thermomolecular pressure effect. There are advantages to the use of a vapour pressure thermometer filled with some ^{3}He for these low temperatures (e.g. below 1.3°K).

For calibrations of secondary thermometers against the vapour

---

* If the velocity of the vapour bubbles is so high that $\frac{1}{2} \rho_L v^2$, where ρ_L is the liquid density and v the velocity of the bubbles, becomes important, the pressure in the bubbles is lowered due to Bernouilli effects. This effect was suggested to us by Prof. K.W. Taconis. The velocity of the bubbles in our helium bath was probably too low for this effect to be of importance.

pressure in which no high accuracy is required, it can be sufficient to use the bath pressure with the hydrostatic head correction. The investigations mentioned above indicate the accuracy of this procedure. A possible remaining discontinuity at the λ-point can be used to correct the data either in the direction as found by Hoare and Zimmerman and by Swim or in the direction as found by us. Further measurements about the temperature gradients in glass dewars are planned by Swim[110] at the Naval Research Laboratory (Washington) and by Oder at the Massachusetts Institute of Technology[111].
We wish to thank Dr. J.R. Clement and Dr. H.H. Plumb for valuable discussions about vapour pressure measurements.

7. Measurements at liquid hydrogen temperatures

Measurements with the glass and metal vapour pressure thermometers were also performed at liquid hydrogen temperatures. As yet the results are not as reproducible as those at helium temperatures. We will only mention that the temperature gradient due to the hydrostatic head becomes very appreciable at the lower hydrogen temperatures (see fig. 46). This makes the use of a vapour pressure thermometer essential for accurate temperature measurements in this temperature region.

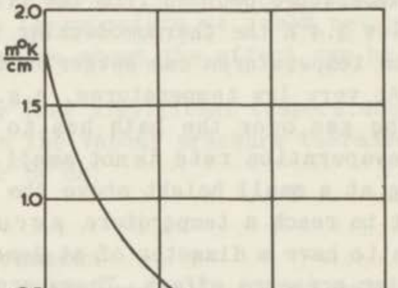

Fig. 46

Temperature gradient g in liquid hydrogen corresponding to the hydrostatic pressure head.

SAMENVATTING

De relaties tussen de verzadigde dampspanningen van vloeibaar ^{4}He en H_2 en de temperatuur (pT relaties) zijn enerzijds van belang omdat ze voor temperatuurmetingen tussen 1 en 5.2°K en tussen 14 en 20.4°K gebruikt worden, anderzijds wegens het verband met andere thermodynamische grootheden van gas en vloeistof. Voor het gebruik als temperatuurschalen is het gewenst, dat deze relaties de thermodynamische temperatuur geven met een nauwkeurigheid van minstens 1°/oo en dat de afgeleide naar de temperatuur tot op enkele promilles goed is. In 1958 werd door het Comité International des Poids et Mesures in Sèvres een nieuwe pT relatie voor ^{4}He aanbevolen (T_{58} schaal). Deze schaal was tot stand gekomen door samenwerking van medewerkers van het Naval Research Laboratorium in Washington en van het Kamerlingh Onnes Laboratorium te Leiden.

In Hoofdstuk II van dit proefschrift worden metingen met een magnetische thermometer ter bepaling van de pT relaties van vloeibaar ^{4}He en H_2 besproken. Als resultaat van de metingen werden kleine verschillen met de bestaande pT relaties gevonden. Verder bleken kleine afwijkingen van de wet van Curie op te treden voor de gebruikte paramagnetische zouten (mangaanammoniumsulfaat en kaliumchroomaluin). Dit illustreert het belang van een nauwkeurige temperatuurschaal: de kleine afwijkingen van de wet van Curie voor kaliumchroomaluin zouden zeer moeilijk te vinden zijn bij gebruik van bijvoorbeeld de 1948 temperatuurschaal.

Hoofdstuk III is gewijd aan de pT relatie voor ^{4}He. Na een inleiding over vroegere temperatuurschalen wordt de bijdrage van de magnetische temperatuurbepalingen tot het tot stand komen van de T_{58} schaal behandeld. Hierna wordt een discussie van deze temperatuurschaal gegeven. In een appendix worden metingen van de dampdruk van vloeibaar helium bij het λ-punt besproken.

In hoofdstuk IV wordt eerst het resultaat der magnetische temperatuurmetingen vergeleken met T_{58}. Daarna worden enkele metingen besproken die gedaan zijn ter nadere bepaling van de Weiss constanten voor kaliumchroomaluin en methylammoniumchroomaluin. In de laatste paragraaf van dit hoofdstuk worden theoretische formules voor de susceptibiliteit besproken en de experimentele resultaten hiermee vergeleken.

Hoofdstuk V is gewijd aan de pT relatie voor waterstof. De magnetische temperatuurbepalingen beschreven in hoofdstuk II en thermodynamische berekeningen worden gebruikt voor het opstellen

van *pT* relaties voor normale- en evenwichtswaterstof. Deze verschillen iets van de thans in gebruik zijnde relaties.
Het laatste hoofdstuk gaat over het meten van temperaturen met dampspanningsthermometers. Eerst worden de eigen meetresultaten besproken. Er blijkt een verschil te bestaan met elders verkregen resultaten. In verband hiermee wordt een beschouwing gegeven over fouten die op kunnen treden bij het meten van temperaturen met dampspanningsthermometers. Aan het eind van dit hoofdstuk worden enige opmerkingen gemaakt over temperatuurmetingen met gebruikmaking van de dampspanning van vloeibare waterstof.

REFERENCES

1. Comptes Rendus des Séances de la dixième Conférence Générale des Poids et Mesures 1954 (Gautier-Villars, Paris 1955).
2. Procès Verbaux des Séances du Comité Consultatif de Thermométrie auprès du Comité international des Poids et Mesures, Session 1954 (Gautier-Villars, Paris 1955).
   Van Dijk, H., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1954, p. T 66.
   Otto, J., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1954, p. T 78.
3. Guggenheim, E.A., Thermodynamics (North-Holland Publ. Comp., Amsterdam 1957).
4. Beattie, J.A., Temperature, its Measurement and Control in Science and Industry II (Reinhold Publ. Corp., New York 1955) Ch. 5.
5. Moser, H., Temperature, its Measurement and Control in Science and Industry II (Reinhold, Publ. Corp., New York 1955) Ch. 7.
6. Van Dijk, H. and Shoenberg, D., Nature 164 (1949) 151.
   Van Dijk, H., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1952, p. T 151.
7. Clement, J.R., Logan, J.K. and Gaffney, J., Phys. Rev. 100 (1955) 743 (Note added in proof). See also refs. 43 and 44.
8. Van Dijk, H. and Durieux, M., Communications from the Kamerlingh Onnes Laboratory, Leiden, Suppl. No. 113c; Physica 24 (1958) 1.
9. Brickwedde, F.G., Physica 24 (1958) p. S128.
   Van Dijk, H., Durieux, M., Clement, J.R. and Logan J.K., Physica 24 (1958) p. S129.
10. Woolley, H.W., Scott, R.B. and Brickwedde, F.G., J. Res. Nat. Bur. Stand. 41 (1948) 379.
11. Hedrich, A.L. and Pardue D.R., Temperature, its Measurement and Control in Science and Industry II (Reinhold Buhl. Corp., New York 1955) Ch. 21.
12. Van Itterbeek, A., Forrez, G., Sluyter, C.G. and Vaes, Miss G., Suppl. au Bull. Inst. internat. Froid, Annexe 1958-1, p. 155.
13. Plumb, H.H. and Edlow, M.H., Rev. sci. Instrum. 30 (1959) 376.
14. Sydoriak, S.G. and Roberts, T.R., Phys. Rev. 106 (1957) 175.
15. ^{3}He Vapour Pressure Tables, distributed by the University of California, Los Alamos Scientific Lab. (1957).
16. Wiersma, E.C., Enige punten uit de ontwikkeling van het temperatuurbegrip (Lecture given in 1936, Nijhoff, 's-Gravenhage).
17. De Klerk, D., Handbuch der Physik XV (Springer Verlag, Berlin 1956).
18. Van Dijk, H., Commun. Leiden, Suppl. No. 112c; Temperature, its Measurement and Control in Science and Industry II (Reinhold Publ. Corp., New York 1955) Ch. 13.
19. Casimir, H.B.G., De Klerk, D. and Polder, D., Commun. Leiden No. 261a; Physica, 's-Grav. 7 (1940) 737.
20. Bleaney, B. and Hull, R.A., Proc. roy. Soc. A 178 (1941) 74.
21. Erickson, R.E. and Roberts, L.D., Phys. Rev. 93 (1954) 957.
22. Kistemaker, J., Commun. Leiden No. 269c; Physica, 's-Grav. 12 (1946) 272.
23. Kistemaker, J., Thesis Leiden (1945).
24. Ambler, E. and Hudson, R.P., J. Res. Nat. Bur. Stand. 56 (1956) 99.
25. Ambler, E. and Hudson, R.P., J. Res. Nat. Bur. Stand. 57 (1956) 23.
26. De Klerk, D. and Hudson, R.P., Private communication.
27. Van Dijk, H. and Durieux, M., Progress in low Temperature Physics II, edited by C.J. Gorter (North-Holland Publ. Comp., Amsterdam 1957) Ch. XIV.

28. Van der Marel, L.C., Van den Broek, J. and Gorter, C.J., Commun. Leiden No. 306a; Physica 23 (1957) 361.
29. Van der Marel, L.C., Thesis Leiden (1958).
30. Weber, S. and Schmidt, G., Commun. Leiden No. 246c (1936).
Keesom, W.H., Helium (Elsevier, Amsterdam 1942) p. 123.
31. Roberts, T.R. and Sydoriak, S.G., Phys. Rev. 102 (1956) 304.
32. Kamerlingh Onnes, H., Commun. Leiden No. 119 (1911).
33. Brickwedde, F.G., Van Dijk, H., Durieux, M., Clement, J.R. and Logan, J.K., J. Res. Nat. Bur. Stand. A (1960) to be published.
34. Abraham, B.M., Osborne, D.W. and Weinstock, B., Phys. Rev. 80 (1950) 366.
35. Berman, R. and Swenson, C.A., Phys. Rev. 95 (1954) 311.
36. Keller, W.E., Phys. Rev. 97 (1955) 1 and 100 (1955) 1790.
Keller, W.E., Phys. Rev. 98 (1955) 1571.
37. Worley, R.D., Zemansky, M.W. and Boorse, H.A., Phys. Rev. 93 (1954) 45.
38. Clement, J.R., Quinnell, E.H., Steele, M.C., Hein, R.A. and Dolecek, R.L., Rev. sci. Instrum. 24 (1953) 545.
39. Clement, J.R., Phys. Rev. 93 (1954) 1420.
Keesom, P.H. and Pearlman, N., Phys. Rev. 98 (1955) 548.
Corak, W.S., Garfunkel, M.P., Satterthwaite, C.B. and Wexler, A., Phys. Rev. 98 (1955) 1699; Westinghouse Research Rep. No. 60-94466-5-R1 (1955).
40. Erickson, R.E., Private communication.
41. Brickwedde, F.G., Suppl. au Bull. Inst. internat. Froid, Annexe 1955-3, p. 608.
42. De Klerk, D., Report added to the "Helium vapour pressure scale T_{L55}" by H. van Dijk and M. Durieux, see ref. 49.
43. Clement, J.R., "Liquid helium vapour pressure temperature scale" distributed at the Baton Rouge (Louisiana) Conference on Low Temperature Physics and Chemistry, December 1955.
44. Clement, J.R., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1958, p. T 21.
45. Ambler, E. and Hudson, R.P., Suppl. au Bull. Inst. Internat. Froid, Annexe 1955-3, p. 605.
46. Clement, J.R., Logan, J.K., and Gaffney, J., Naval Research Lab. Rep. No. 4542 (1955).
47. Dana, L.I. and Kamerlingh Onnes, H., Commun. Leiden. No. 179c; Proc. roy. Acad., Amsterdam 29 (1926) 1051.
48. Berman, R. and Poulter, J., Phil. Mag. 43 (1952) 1047.
49. Van Dijk, H. and Durieux, M., "Helium vapour pressure scale T_{L55}", distributed in April 1956. This report has been published completely in Procès Verbaux du Comité Consultatif de Thermométrie, Session 1958, p. T 165.
50. Kamerlingh Onnes, H. and Boks, J.D.A., Commun. Leiden No. 170b; Rapp. et Comm. 4e Congr. int. du Froid, London 1924,
51. Keesom, W.H. and Keesom, Miss A.P., Commun. Leiden No. 224d; Proc. roy. Acad., Amsterdam 35 (1932) 320.
52. Kilpatrick, J.E., Keller, W.E. and Hammel, E.F., Phys. Rev. 97 (1955) 9.
53. Kramers, H.C., Wasscher, J.D. and Gorter, C.J., Commun. Leiden No. 288c; Physica 18 (1952) 329.
54. Keesom, W.H. and Keesom, Miss A.P., Commun. Leiden No. 221a; Proc. roy. Acad., Amsterdam 35 (1932) 736.
Keesom, Miss A.P., Thesis Leiden (1936).
Keesom, W.H. and Clusius, K., Commun. Leiden No. 219e; Proc. roy. Acad., Amsterdam 35 (1932) 307.
55. Dana, L.I. and Kamerlingh Onnes, H., Commun. Leiden No. 179d; Proc. roy. Acad., Amsterdam 29 (1926) 1061.
56. Keller, W.E., Nature 178 (1956) 883.
57. Berman, R., Cooke, A.H. and Hill, R.W., Annual Rev. of phys. Chem. 7 (1956) 1.
58. Hill, R.W. and Lounasmaa, O.V., Phil. Mag. 2 (1957) 143.
Lounasmaa, O.V., Thesis Oxford (1958).

59. Fairbank, W.M., Buckingham, M.J. and Kellers, C.F., Bull. Amer. phys. Soc. 2 (1957) 183.
60. Kerr, E.C., J. chem. Phys. 26 (1957) 511.
61. Van Dijk, H. and Durieux, M., Proc. fifth internat. Conf. on Low Temp. Phys. and Chem., Madison 1957 (University of Wisconsin Press, Madison 1958) p. 192.
62. Clement, J.R., Proc. fifth internat. Conf. on Low Temp. Phys. and Chem., Madison 1957 (University of Wisconsin Press, Madison 1958) p. 187. See also ref. 44.
63. Brickwedde, F.G., Physics Today 11 (1958) 23.
Brickwedde, F.G., A status Report on a standard Scale from 1-5.2°K (July 24, 1957) unpublished.
64. Edeskuty, F.J. and Sherman, R.H., Proc. fifth internat. Conf. on Low Temp. Phys. and Chem., Madison 1957 (University of Wisconsin Press, Madison 1958) p. 102.
65. Edwards, M.H., Canad. J. Phys. (1958) 884.
66. Edwards, M.H., Phys. Rev. 108 (1957) 1243.
Edwards, M.H., Physica 24 (1958) p. S138 (Proc. Kamerlingh Onnes Conf., Leiden 1958).
67. Clement, J.R., Private communication.
68. Clement, J.R., Logan, J.K. and Swim, R.T., Private communication.
69. Van Dijk, H. and Durieux, M., Commun. Leiden, Suppl. No. 115a; Physica 24 (1958) 920.
70. Gorter, C.J. and Brickwedde, F.G., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1958, p. T 188.
Van Dijk, H., Durieux, M., Clement, J.R. and Logan, J.K, Procès Verbaux du Comité Consultatif de Thermométrie, Session 1958, p. T 190.
71. Schmidt, G. and Keesom, W.H., Commun. Leiden No. 250b and c; Physica, 's-Grav. 4 (1937) 963 and 971.
Schmidt, G., Thesis Leiden (1938).
72. Kistemaker, J. and Keesom, W.H., Commun. Leiden No. 269b; Physica, 's-Grav. 12 (1946) 227.
73. Clement, J.R., Private communication.
74. Berman, R., Private communication.
75. Berman, R. and Mate, C.F., Phil. Mag. 3 (1958) 461.
76. Keesom, W.H., Helium (Elsevier, Amsterdam 1942) Table 2.14.
77. Van Dijk, H., Procès Verbaux du Comité Consultatif de Thermométrie, Session 1958, p. T 61.
78. Van Dijk, H., Progress in Cryogenics, edited by K. Mendelssohn (Heywood & Co. London 1960).
79. Long, E. and Meyer, L., Phys. Rev. 83 (1951) 860.
80. Dash, J.G. and Dean Taylor, R., Phys. Rev. 99 (1955) 598.
81. Winkel, P., Thesis Leiden (1954) Stelling IX.
82. Bleaney, B. and Ingram, D.J.E., Proc. roy. Soc. A 205 (1951) 336.
83. Cooke, A.H., Progress in low Temperature Physics I, edited by C.J. Gorter (North-Holland Publ. Comp., Amsterdam 1957 Ch. XII.
84. Van Vleck, J.H., J. chem. Phys. 5 (1937) 320.
85. Hebb, M.H. and Purcell, E.M., J. chem. Phys. 5 (1937) 338.
86. O'Brien, Mary C.M., Phys. Rev. 104 (1956) 1573.
87. Baker, J.M., Proc. phys. Soc. (London) 69 (1956) 633.
88. Bleaney, B., Proc. roy. Soc. A 204 (1951) 203.
89. Beun, J.A., Miedema, A.R. and Steenland, M.J., Commun. Leiden No. 315a; Physica 25 (1959) 399.
90. Bots, G.J.C., Thesis Leiden (1959); Physica, to be published.
91. Miedema, A.R., Van den Broek, J., Postma, H. and Huiskamp, W.J., Commun. Leiden No. 318a; Physica 25 (1959) 1177.
92. Hoge, H.J. and Arnold, R.D., J. Res. Nat. Bur. Stand. 47 (1951) 63.
93. Grilly, E.R., Los Alamos Report LADC-773 (July 11, 1950).
94. White, D., Friedman, A.S. and Johnston, H.L., J. Amer. chem. Soc. 72 (1950) 3927.
95. Varekamp, F.H. and Beenakker, J.J.M., Commun. Leiden No. 316c; Physica 25 (1959) 889.

96. Beenakker, J.J.M., Varekamp, F.H. and Knaap, H.F.P., Commun. Leiden No. 319a; Physica 26 (1960) to be published.
97. Johnston, H.L. and White, D., Trans. Amer. Soc. mech. Engin. (1950) p. 785.
98. Simon, F. and Lange, F., Z. Phys. 15 (1923) 312.
99. Johnston, H.L., Clarke, J.T., Rifkin, E.B. and Kerr E.C., J. Amer. chem. Soc. 72 (1950) 3933.
100. Clusius, K. and Hiller, K., Z. physik. Chem. B 4 (1929) 158.
101. Moesson, G.W. and Aston, J.G., Private communication. Moesson, G.W., Aston, J.G. and Ascah, R.G., J. chem. Phys. 22 (1954) 2096.
102. Barber, C.R., Proc. Xth internat. Congr. of Refrig. (Copenhagen 1959) to be published in Bull. Inst. internat. Froid.
103. Durieux, M. and Van Dijk, H., Proc. Xth internat. Congr. of Refrig. (Copenhagen 1959) to be published in Bull. Inst. internat. Froid.
104. Hoare, F.E. and Zimmerman, J.E., Rev. sci. Instrum. 30 (1959) 184.
105. Plumb, H.H., Proc. Xth internat. Congr. of Refrig. (Copenhagen 1959) to be published in Bull. Inst. internat. Froid.
106. Swim, R.T., Paper presented at the Cryogenic Engin. Conf. (Berkeley 1959), preprint.
107. White, G.K., Experimental Techniques in low Temperature Physics (Clarendon Press, Oxford 1959).
108. Grassmann, P,, Kältetechnik 10 (1958) 301.
109. Taconis, K.W., Beenakker, J.J.M., Nier, A.O.C. and Aldrich, L.T., Commun. No. 279a; Physica, 's-Grav. 15(1949) 733. Kramers, H.A., Commun. Suppl. No. 100a; Physica, 's-Grav. 15(1949) 971.
110. Swim, R.T., Private communication.
111. Annual Res. Rep. Mass. Inst. of Technology, Lab. of chem. and solid-state Phys. (July, 1959) p. 29.