ON THERMOMETRY BETWEEN 63 AND 273.15°K

MAHMOUD RASHAD MOUSTAFA MOUSSA

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PROEFSCHRIFT

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IN DE WISKUNDE EN NATUURWETENSCHAPPEN
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MAHMOUD RASHAD MOUSTAFA MOUSSA

Geboren te Mit-Bera, Egypte, V.A.R. in 1937

DRUKKERIJ „LUCTOR ET EMERGO" — LEIDEN

Promotor: Prof. Dr C. J. Gorter

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

To my wife

To Amr, Amina and Hanan

Promotor: Prof. Dr C. J. Gorter

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

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

My primary education took place in Mit-Bera, Monofiah, Egypt, where I was born. After finishing my studies at Benha Secondary School at Benha, Kaliubiah, in 1956, I started my study at the Faculty of Science of Ain-Shams University in Cairo. In 1960, I obtained a Bachelor of Science degree (B.Sc.) with distinction, majoring in physics. After that I worked as an assistant in the department of physics at the same University.

In April 1961 I obtained a scholarship from the National Research Centre in Cairo, U.A.R., to study for the doctor degree in thermometry and calorimetry.

In September 1961 I came to Europe. At first I studied under the supervision of Professor J. S. Rowlinson at the Chemical Engineering Department of the Imperial College of the University of London. I then joined the Kamerlingh Onnes Laboratory of the University of Leiden in August 1962, where I studied under the guidance of Professor C. J. Gorter and the direct supervision of Dr. H. van Dijk and Dr. M. Durieux. On January 14, 1964 I obtained the degree of Doctorandus in physics at the University of Leiden.

During my study at Leiden I had the benefit of the cooperation of many members of the laboratory.

My colleagues in the thermometry section: Messrs. H. ter Harmsel, C. van Rijn, E. H. Vossepoel, H. Kossen, Z. El-Hadi, J. L. Tiggelman, and A. A. M. Thijssen helped on many occasions and in particular Mr. R. Muijlwijk cooperated in part of the measurements and participated in many discussions. Mr. W. Nuy and Mr. J. A. Dorrepaal performed the calculations with the computer of the Mathematical Institute of the University.

I would like to mention Messrs. H. Kuipers, B. Kret, L. W. Muller, L. Neuteboom, E. S. Prins and J. Turenhout for their valuable contributions to the construction of the apparatus and Mr. W. F. Tegelaar for making the drawings. The administrative staff aided in typing the manuscript.

Professor R. A. Aziz kindly read the manuscript and improved the language.

I am very much obliged to my wife for helpful cooperation.

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CHAPTER I

INTRODUCTION

1. General remarks

Temperatures in the low temperature range from 273.15°K down to about 10°K are frequently measured with platinum resistance thermometers. To make the results comparable it is desirable that all temperatures can be reduced to a same scale. To enable interpretation of the temperature dependence of measured physical quantities, it is desirable that the common scale be in close agreement with the thermodynamic scale. To realize this for the temperature region mentioned above, individual platinum thermometers have been compared (directly or indirectly) with the helium gas thermometer at several laboratories. For high quality platinum resistance thermometers the temperature dependence of the reduced resistance, $R(T)/R(273.15°\mathrm{K})$, is nearly the same as long as the temperatures are not too low (e.g. $> 50°\mathrm{K}$). But differences become more and more appreciable at lower temperatures. To realize reasonable agreement between different platinum thermometers it is desirable that the average temperature coefficient of the resistance between 0°C and 100°C be at least $0.003920°\mathrm{C}^{-1}$ for thermometers used only above 55°K and at least $0.003925°\mathrm{C}^{-1}$ for thermometers that have to be used also below 55°K. But even if these conditions were fulfilled appreciable differences can occur between different platinum thermometers and calibrations are required. The calibrations of secondary platinum resistance thermometers consist of direct or indirect comparisons with platinum thermometers (primary standards) which have been compared with a gas thermometer. Several institutes dispose of primary standards. To make sure that the primary standards of different institutes are in close agreement with each other and to realize the establishment of a generally acceptable common scale, platinum thermometers calibrated at different institutes have been compared with each other.

Individual scales can be maintained for a long time with thermometers calibrated directly or indirectly against a gas thermometer and the scales can be compared with each other, and eventually reduced to a same scale, but the accuracy of the reproduction of the scale will depend on the stability of the primary standards. The need for accurate reproduction will make not only repeated comparisons of the scales necessary but also, after a long period of time, recalibration of the primary standards against a gas thermometer. To avoid this and to enable a well-equipped laboratory to calibrate its own thermometers, standard functions (and tables) for the reduced resistance as a function of temperature are required. When a platinum thermometer is calibrated at a number of fixed points its reduced resistance can be found by interpolation between the fixed points using the standard functions (or tables).

In the temperature region between 0 and –183°C the Callendar-Van Dusen relation:

$$R(t)/R(0^\circ\mathrm{C}) = 1 + \alpha t - \alpha\delta \frac{t}{100}\left(\frac{t}{100} - 1\right) - \alpha\beta \frac{t^3}{100^3}\left(\frac{t}{100} - 1\right)$$

is used as a standard function. R is the resistance and t the international temperature in °C. The values for the constants α, δ and β for each thermometer are obtained from measurements at four fixed points. These fixed points are three boiling points and one triple point of pure substances. Such points can be realized very accurately. They are also very important for the improvement and extension of the International Practical Temperature Scale (IPTS) since they enable us to become independent from the stability and lifetime of primary standard thermometers. Between 273.15 and 10°K many fixed points are available, but the knowledge of the temperatures of the fixed points is only in a few cases sufficiently accurate for present requirements. Therefore redetermination of several fixed points is desirable.

Instead of fixed points the pressure of the saturated vapour of a condensed gas may be measured. This pressure is a single-valued function of the thermodynamic temperature that changes rapidly with temperature. Accurate thermodynamic temperatures can be derived from the vapour pressure measurements in those temperature ranges, where the pressure is not too large or too small, as soon as the *p-T* relation is known with sufficient accuracy. In the temperature range between 55 and 90°K the vapour pressure-temperature relations of oxygen and nitrogen are very important.

2. Summary of contents

This thesis deals with:

a. Measurements of the temperature dependence of the pressure of the saturated vapour of liquid nitrogen between 63 and 85°K.

b. Evaluation of a vapour pressure-temperature relation for liquid nitrogen that is consistent with available thermodynamic data and with the best available information from gas thermometry.

c. Evaluation of accurate data for the boiling point and triple point of nitrogen.

d. Comparison of standard platinum resistance thermometers which have been calibrated against a gas thermometer at the National Physical Laboratory (NPL) in Teddington with standard platinum resistance thermometers which have been calibrated against a gas thermometer at the Kamerlingh Onnes Laboratory (KOL) in Leiden.

e. Comparison of 13 platinum resistance thermometers of different origin and quality between 63 and 373°K.

3. The vapour pressure-temperature relation for liquid nitrogen between 63 and 85°K

The pressure *p* of the saturated vapour of a condensed gas is a function of the thermodynamic temperature *T* and changes rapidly with temperature. Once the *p-T* relation is known with high precision, accurate thermodynamic temperatures can be obtained conveniently from vapour pressure measurements using a suitable vapour pressure thermometer.

The vapour pressure-temperature relation of nitrogen has been measured by a rather large number of investigators. It has been measured in different ways using thermocouples, platinum resistance thermometers, and gas thermometers. From an analysis of all the published experimental data it has been found that the different experimental data do not agree very accurately. Also, the existing data for the boiling point and the triple point of nitrogen show rather large differences. Because the p-T relation of liquid nitrogen is important in low temperature thermometry it seemed desirable to carry out a new accurate determination of it.

The p-T relation of liquid nitrogen can be obtained from direct measurements of p and T, and from thermodynamic calculations. The accuracy of the results obtained from direct measurements of p and T is limited mainly by the inaccuracies of temperature measurements with the gas thermometer. The use of a thermodynamic p-T relation helps to avoid, or to eliminate, irregularities in the results obtained with the gas thermometer. The accuracy of the calculated p-T relation is limited by the uncertainties in the data for the thermodynamic quantities which are used in the calculations. An accurate p-T relation was obtained by representing our results obtained from p and T measurements in an equation that satisfies the requirements of thermodynamics within the limits of the accuracy of the available experimental data.

The study of the p-T relation for liquid nitrogen is of interest in several respects:

a. This relation can be used in thermometry to derive temperatures from measured vapour pressures in order to calibrate secondary platinum resistance thermometers accurately between 63 and 85°K.

b. If the p-T relation is known accurately, temperature scales, which involve the use of platinum thermometers calibrated against gas thermometers, can be checked by measuring the vapour pressure as a function of the temperature in such a scale.

c. A comparison of the p-T relation obtained from thermodynamic calculations with the p-T relation obtained from direct measurements of p and T is an excellent way to check the consistency of the thermodynamic quantities.

Vapour pressures can be measured using one of the following arrangements:

a. In the first arrangement, fig. 1*a*, the vapour pressure over a nitrogen bath, boiling under atmospheric pressure or under controlled pressure, is measured. In such an arrangement the occurrence of a temperature gradient in the nitrogen bath may make the recorded vapour pressure a rather poor indication of the true temperature at points within the liquid. Determinations of vapour pressures in this way yield temperatures which are insufficiently accurate for many experiments.

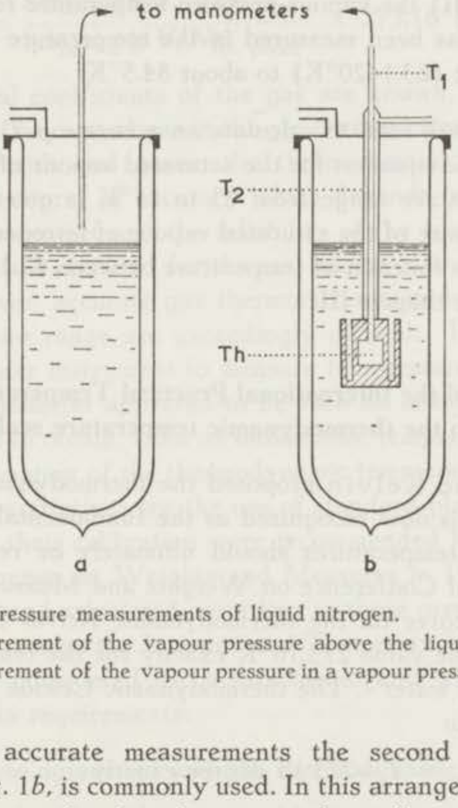

Fig. 1. Vapour pressure measurements of liquid nitrogen.
a. Measurement of the vapour pressure above the liquid nitrogen bath.
b. Measurement of the vapour pressure in a vapour pressure thermometer.

b. For fairly accurate measurements the second arrangement, shown in fig. 1*b*, is commonly used. In this arrangement a copper block is immersed in liquid nitrogen. A small cavity within the copper block forms the reservoir *Th* of a vapour pressure thermometer into which pure nitrogen is condensed. The tube T_1 connects the vapour pressure thermometer reservoir *Th* to a manometer system. T_1 is surrounded by another tube T_2, which prevents condensation of the gas in T_1. The space between the walls of T_1 and T_2 can be evacuated or filled with some gas for heat exchange. Nitrogen gas is admitted to Th until it is partially filled with liquid. During measurements the liquid and its vapour must be in equilibrium. Additional holes in the copper block around Th allow insertion of platinum resistance thermometers, thermocouples, gas thermometers etc. The normal region for the use of the vapour pressure of nitrogen for temperature measurements is between 63 and 77.34°K. But in our experiments (chapter III) the vapour pressure-temperature relation of liquid nitrogen has been measured in the temperature range from the triple point (63.1420°K) to about 84.5°K.

The procedure used to calculate an accurate p-T relation from a thermodynamic equation for the saturated vapour of liquid nitrogen in the temperature range from 63 to 85°K is given in chapter II. How the pressure of the saturated vapour of nitrogen was measured accurately as a function of temperature between 63.1420 and 84.5°K is described in chapter III.

4. Relation of the International Practical Temperature Scale (IPTS) to the thermodynamic temperature scale

In 1854 Lord Kelvin proposed the thermodynamic temperature scale [1] which is now recognized as the fundamental scale to which all measured temperatures should ultimately be referable. At the Tenth General Conference on Weights and Measures in 1954, the size of the degree on the thermodynamic Kelvin Scale was fixed by adopting the value 273.16°K exactly for the temperature at the triple point of water [2]. The thermodynamic Celcius scale is defined by the relation:

$$t_{\mathrm{th}} = T - 273.15 \text{ degree exactly}$$

where t_{th} is the thermodynamic Celsius temperature and T the thermodynamic Kelvin temperature.

Over a wide temperature range, the thermodynamic temperature can be measured with a gas thermometer. The procedure is in principle the following: A bulb containing a known amount of gas is brought into thermal equilibrium with the system whose temperature T is desired. The quantity pV/N is determined, where p is the pressure of the gas, V the inner volume of the bulb and N the number of moles of the gas. 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 triple point of water; this results in a value $\lim_{N\to 0}(pV/N)_{\text{tr. point}}$. The thermodynamic temperature of the original system is then found from the relation:

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

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

In practice, with real gases, the thermodynamic scale can be realized with a degree of accuracy which depends on the accuracy of the gas thermometer and the reliability of the corrections which are applied to data obtained for the real gas to account for its non-ideality. However, accurate gas thermometer measurements over a wide temperature range are exceedingly difficult. This led to the need for an easier instrument to measure temperatures. A platinum resistance thermometer appeared to be such an instrument[3]. It has to be calibrated to obtain, from its indications, temperatures that are a good approximation of the thermodynamic temperature. Comparatively simple prescriptions for the use of standard platinum thermometers and for their calibration were recommended by the Seventh General Conference on Weights and Measures in 1927. Temperatures measured and calculated according to those prescriptions were called temperatures on the International Temperature Scale (ITS)[4]. The scale was considered to be provisional and was intended to realize two main requirements:

a. To be in close agreement with the thermodynamic scale .

b. To be reproducible within reasonable limits.

The definition of the ITS between 630.5 and –183°C required measurements of standard platinum thermometers at four fixed points. These measurements provide the data to calculate four constants, which are to be used in two interpolation formulae, one formula to calculate temperatures between 0 and 630.5°C and the other to calculate temperatures between 0 and −182.97°C. The formulae define the resistance of platinum as a function of the international temperature. The four fixed points and their defined temperatures on the ITS are:

1. The boiling point of sulphur at 444.60°C.
2. The boiling point of water at 100.000°C.
3. The ice point at 0°C.
4. The boiling point of oxygen at −182.97°C.

In 1954[5], the ice point was replaced as a fixed point by the triple point of water which is more reproducible. The temperature of the triple point of water on the international (Celsius) scale was defined as 0.0100°C[*] and it was recommended in 1960 to use the melting point of zinc[7] (419.505°C) instead of the boiling point of sulphur. The interpolation formula of Callendar-Van Dusen[8] for the temperature range between 0 and −183°C, can be written in the form:

$$t = 100\frac{R_t - R_0}{R_{100} - R_0} + \delta\frac{t}{100}\left(\frac{t}{100} - 1\right) + \beta\left(\frac{t}{100}\right)^3\left(\frac{t}{100} - 1\right)$$

where t is the international (Celsius) temperature and the four constants R_0, R_{100}, δ and β are to be determined by calibration at the four fixed points. In addition to the international (Celsius) scale there is an international Kelvin scale defined by the relation:

$$T_{\text{int}} = t + 273.15 \text{ degree exactly}$$

where T_{int} is the international Kelvin temperature.

At the time of the establishment of the ITS (1927), it was expected to be in agreement with the thermodynamic scale to within about 0.04°C between 0 and −183°C. The thermodynamic scale, as determined by a gas thermometer, was compared with the ITS at the Physikalisch Technische Reichsanstalt (PTR)[9] in Berlin and at the Kamerlingh Onnes Laboratory (KOL)[10] in Leiden. Both labo-

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[*] A revision of the ITS of 1927 has been published in 1960[6]. It has been given the title International Practical Temperature Scale of 1948 (Échelle Internationale Pratique de Température de 1948, édition amendée de 1960).

ratories noted a maximum deviation of about 0.04°C near –80°C. But in the neighbourhood of –115°C the deviation $t_{th} - t_{int}$ changed sign and became negative according to the Leiden results, whereas it remained positive according to the Berlin results. Although the Leiden results showed a smaller spread of the individual points in the $t_{th} - t_{int}$ vs. t plots and their estimated accuracy was about 4 m°C, a number of difficulties had to be considered and overcome before agreement about improvement of the ITS in this region could be expected. Keesom and Dammers (the Leiden results) made measurements at many temperatures between 0 and about –153°C using five platinum resistance thermometers and a gas thermometer. Moreover, they compared their five thermometers at the boiling point of oxygen with a gas thermometer, but they did not make measurements between about –153 and –183°C and below —183°C. This led to a difficulty in the neighbourhood of –183°C. Although it became evident soon after 1927 that the definition of the ITS could not be used for reasonably accurate extrapolation below —183°C, it proved to be difficult to give a more accurate alternative of the Callendar-Van Dusen relation. It became clear that the Callendar-Van Dusen relation could not give correct values for the first and second derivatives of the resistance with respect to temperature at –183°C for it was already known from earlier results[11] for $W = R(t)/R(0°\mathrm{C})$ versus t obtained for temperatures down to –258°C that for reasonably pure platinum $\mathrm{d}W/\mathrm{d}t$ has to show a maximum in the neighbourhood of –187°C. According to the Callendar-Van Dusen relation $\mathrm{d}W/\mathrm{d}t$ should increase more and more rapidly with decreasing temperature.

Since near –187°C $\mathrm{d}^2W/\mathrm{d}t^2$ has to become zero and –187°C is so close to –183°C, it is likely that the Callendar-Van Dusen relation gives too large a value for $\mathrm{d}W/\mathrm{d}t$ or that $\mathrm{d}W/\mathrm{d}t_{int} > \mathrm{d}W/\mathrm{d}t_{th}$ and $\mathrm{d}(t_{th} - t_{int})/\mathrm{d}t_{int}$ is positive at –183°C. The same would have been expected also if only the Berlin data were available. According to the interpolation of the deviation curves $t_{th} - t_{int}$ vs. t_{int} suggested by Keesom and Dammers, however, $\mathrm{d}(t_{th} - t_{int})/\mathrm{d}t_{int}$ is negative. This difficulty regarding the improvement of the scale between 0 and –183°C could not be solved without new measurements with the gas thermometer. Such measurements have been made recently by Barber and Horsford[12] at the National Physical Laboratory (NPL) in England. Their results confirmed the results of Keesom and Dammers between 0 and –153°C and provided also information for temperatures between –153°C and –183°C and below –183°C. From the latter information it is evident that at –183°C the derivative $d(t_{th} - t_{int})/dt_{int}$ is positive and that the deviation curve $t_{th} - t_{int}$ versus t_{int} passes the zero line not only at 0°C, at about –115°C and at –183°C, but also between —153 and –183°C. The fact that scale differences found at KOL and NPL are in agreement with each other within experimental error in spite of the fact that the platinum used for Barber and Horsford's thermometers was considerably purer than that used by Keesom and Dammers is an indication that, at least for well treated and annealed platinum thermometers, there exists a simple relation between the reduced resistance differences if the platinum wire is sufficiently pure. Chapter IV of this thesis will deal with intercomparisons between such old and recent platinum resistance thermometers, which are of different origin and quality, in the temperature range from about 65 to 273.15°K. We used in this experiment three platinum thermometers out of the five platinum thermometers which had been calibrated by Keesom and Dammers against their constant volume helium gas thermometer at Leiden in 1935, and two platinum thermometers manufactured by H. Tinsley and Co., Ltd., London, England. These two thermometers had been calibrated at the NPL on the NPL scale in the temperature range between 10 and 90°K in 1962 and in the temperature range between 90 and 273.15°K in February 1965 *.

The aim of this part of our experiments is firstly, to get additional information about the agreement between the results obtained by Keesom and Dammers and those obtained at NPL and secondly to measure the temperature dependence of the differences in reduced resistance for thermometers of different origin and quality.

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* We would like to express our sincere thanks to Mr. C. R. Barber at the National Physical Laboratory, Teddington, for his kind cooperation in calibrating the thermometers on the NPL scale.

CHAPTER II

THE THERMODYNAMIC VAPOUR PRESSURE-TEMPERATURE RELATION OF LIQUID NITROGEN

1. A thermodynamic equation for the p-T relation

The vapour pressure-temperature relation for liquid nitrogen suitable for practical use in thermometry can not only be obtained from direct vapour pressure and temperature measurements, but can also be computed from thermal and p-V-T data of the gaseous and liquid states using the following thermodynamic relation [13]:

$$\ln \frac{p}{p_1} = \left\{\frac{L(T_1)}{RT_1} - 1 - \varkappa_1\right\}\left(1 - \frac{T_1}{T}\right) - \ln \frac{T_1}{T} + \int_{T_1}^{T} \frac{C_{V_i} - C_L}{RT} \mathrm{d}T - \frac{1}{RT}\int_{T_1}^{T} \left(C_{V_i} - C_L\right)\mathrm{d}T + \frac{1}{RT}\int_{T_1}^{T} V_L \frac{\mathrm{d}p}{\mathrm{d}T}\mathrm{d}T + \varepsilon - \varepsilon_1 \qquad (1)$$

where:

p is the pressure at saturation at an arbitrary temperature T and p_1 is the pressure at the temperature T_1

$L(T_1)$ is the molar heat of vaporization at the temperature T_1, e.g. at the normal boiling point of liquid nitrogen

R is the gas constant, which is fairly well known and equal to [14] 1.98727 cal/mole °K

C_L is the molar heat capacity of the liquid along the saturation line

V_L is the molar volume of the liquid at saturation pressure

C_{V_i} is the molar heat capacity of the gas at constant volume V_i, where this volume is chosen so large that the gas behaves as an ideal gas. (C_{V_i} can be taken equal to $\frac{5}{2}$ R for nitrogen in the temperature region considered). η and ε are corrections of the preceding terms due to the non-ideality of the gas. η_1 and ε_1 are the values of η and ε respectively, at the temperature T_1.

We used in these calculations the equation of state for the gas in the form:

$$PV = RT\left(1+\frac{B}{V}\right)$$

in which V is the molar volume of the gas at the pressure P and the temperature T, and B is the second virial coefficient of the gas.

In this case:

$$\varepsilon = \ln\frac{pV_\mathrm{G}}{RT} - \frac{2B}{V_\mathrm{G}},$$

$$\eta = \frac{B}{V_\mathrm{G}} - \frac{T}{V_\mathrm{G}}\frac{\mathrm{d}B}{\mathrm{d}T}$$

where V_G is the molar volume of the gas at saturation pressure.

Using some abbreviations, eq. (1) can be written as follows:

$$\ln\frac{p}{p_1} = A\left(1-\frac{T_1}{T}\right) + \ln\frac{T}{T_1} - I_1 + I_2 + I_3 + \varepsilon - \varepsilon_1 \tag{2}$$

where:

$$A = \frac{L(T_1)}{RT_1} - 1 - \eta_1$$

$$I_1 = \int_{T_1}^{T} \frac{\mathrm{C_L} - C_{V_\mathrm{i}}}{RT}\,\mathrm{d}T$$

$$I_2 = \frac{1}{RT}\int_{T_1}^{T}\left(\mathrm{C_L} - C_{V_\mathrm{i}}\right)\mathrm{d}T$$

$$\text{and}\quad I_3 = \frac{1}{RT}\int_{T_1}^{T} V_\mathrm{L}\,\frac{\mathrm{d}p}{\mathrm{d}T}\,\mathrm{d}T.$$

Eq. (1) shows the influence of different physical quantities in the expression for ln p. It is suitable for use in thermometry to obtain thermodynamic temperatures from vapour pressure measurements, when the terms in this equation can be calculated with sufficient accuracy. Eq. (1) or (2) was applied to compute p-T values for liquid nitrogen from 63 up to 85°K.

2. The principal term in equation (2)

The main term in eq. (2) is:

$$A\ (1 - T_1/T) = [\{L\,(T_1)/RT_1\} - 1 - \varkappa_1](1 - T_1/T)\ .$$

Therefore it is necessary to know the coefficient A with a high accuracy in order to obtain an accurate p-T relation. Since $L(T_1)/RT_1$—1 is very much larger than $\varkappa_1$, it is necessary to know $L(T_1)$ with high precision, e.g. better than 0.1%, while a precision of a few percent is sufficient for $\varkappa_1$. Also the terms I_2—I_1, I_3 and ε—ε_1, have to be obtained with sufficient accuracy from available experimental information. When all terms in eq. (2) can be calculated with sufficient accuracy, the equation can be used to obtain an adequate representation of the p-T relation that may be used for defining the temperature scale in the region considered.

The heat of vaporization at the normal boiling point of nitrogen is known more accurately than at other temperatures and it has been measured more frequently. Therefore it is advisable to take for T_1 in eq. (1) or (2), the temperature of the normal boiling point of nitrogen. The heat of vaporization at the normal boiling point of nitrogen has been measured by Dewar[15], Alt[16], Eucken[17], Dana[18], Millar and Sullivan[19], Giauque and Clayton[20], and Furukawa and McCoskey[21]. Of all the experimental data the values 1332.9 and 1336.6 cal/mole given by Giauque and Clayton, and by Furukawa and McCoskey repectively, are considered to be of higher precision than the others. But in spite of that, the difference between them is still 3.7 cal/mole (0.28%). When we use the average value (1334.8 cal/mole) of these two experimental values for $L(T_1)$, this may be still less accurate than is desirable for the precision of our calculations. In fact, for a provisional calculation of the thermodynamic p-T values for liquid nitrogen from 63 up to 85°K we used the value 1334.8 cal/mole for $L(T_1)$. But later on we calculated the coefficient A from eq. (2) using our measured p and T values for the boiling point (77.3385°K and 760.000 mm Hg, 0°C and standard gravity 980.665 cm/s^2) and the triple point (63.1420°K and 93.921 mm Hg, 0°C and standard gravity 980.665 cm/s^2), see chapter III sections 8*b* and 8*c*. For the correction terms I_1, I_2, I_3, ε and ε_1, we chose values obtained from the available experimental data (see section 3).

When the coefficient A is deduced in this way, it is possible to obtain a value for the heat of vaporization, $L(T_1)$, of liquid nitrogen at the normal boiling point since

$$L(T_1) = (A + 1 + \varkappa_1)\, RT_1$$

$\varkappa_1$ is the value of $\varkappa$ for $T = T_1$. This correction due to the non-ideality of the gas can be deduced with a reasonable accuracy from the available experimental data. It is equal to 0.119 when Van Itterbeek's formula [22] for B is used.

T_1 is the boiling point of nitrogen and is equal to 77.3385°K. The value of $L(T_1)$ deduced in this way, is 1334.8 cal/mole, which is found to be in agreement with the average value, 1334.8 cal/mole, deduced from the experimental data of Giauque and Clayton, and of Furukawa and McCoskey.

3. The correction terms

a. The most important correction term in eq. (1) is $\varepsilon - \varepsilon_1$. To calculate ε and ε_1 a provisional p-T relation and accurate values of the second virial coefficient, B, are required. Up to 85°K it is sufficient to describe the non-ideality of the gas at the saturation pressure by means of the second virial coefficient.

The second virial coefficient of nitrogen has been determined as a function of temperature by a number of investigators [23-30]. The accuracy of the available experimental data is not better than a few percent. B has been calculated also using a Lennard-Jones 6-12 potential [31] and taking for its parameters the values given by Ziegler and Mullins [32], $\varepsilon/k = 90.467$°K and $b_0 = 76.869$ cm^3 mole^{-1}. The data given by Cath and Kamerlingh

Onnes, Keesom and Van Lammeren, and by Van Itterbeek and Forrez and those calculated with a Lennard-Jones function have been compared. The representation of B as a function of T given by Van Itterbeek et al. is chosen for use in our calculation of the p-T relation because it is in good agreement, in the temperature region under consideration, with the average of all data mentioned above. This representation of the $B(T)$ data is:

$$10^3B = 0.200 + 3.803\frac{10^2}{T} - 20.371\frac{10^4}{T^2} + 13.007\frac{10^6}{T^3} - 3.760\frac{10^8}{T^4} \quad (3)$$

where B, the second virial coefficient, is in amagat units and T is in °K. (1 amagat unit of volume for nitrogen = 22404.5 cm^3/mole.) Equation (3) can be used between 65 and 150°K.

For the calculation of V_G, the pressure p has to be taken from a provisional p-T relation. As a provisional p-T relation we used Armstrong's equation[33] (see chapter III section 2).

b. The sum of the terms $\int\limits_{T_1}^{T} \{(C_{V_i} - C_L)/RT\}\,dT$ and

$- (1/RT) \int\limits_{T_1}^{T} (C_{V_i} - C_L)dT$ contributes only a small amount to ln p. But each of them apart would contribute a larger amount. To calculate these two terms, C_{V_i} has been taken equal to $\frac{5}{2}R$.

To obtain an accurate information on the heat capacity of liquid nitrogen at the saturation pressure (C_L), in the temperature range from the triple point up to 85°K, we considered all available experimental data.

The heat capacity of condensed nitrogen has been measured by Giauque and Clayton in the range from 15.82 up to 77.74°K, by Wiebe and Brevoort[34] in the range from 79.17 up to 116.99°K, by Clusius[35] in the range from 10.42 up to 73.5°K, by Keesom and Kamerlingh Onnes[36] in the range from 15.27 up to 76.49°K and by Eucken[17] in the range from 16.5 up to 72.7°K. These experimental data are represented, in the temperature range considered, in fig. 1. The data of Clusius are consistently higher than those of Giauque and Clayton and the average difference between them is 0.15 ± 0.01 cal/mole °K except for one point at 68.4°K. Eucken's data are lower than those of Giauque and Clayton, and the average difference between them is 0.15 ± 0.07 cal/mole °K. The data of Keesom and Kamerlingh Onnes scatter over a wide range. The data of Wiebe and Brevoort and those of Giauque and Clayton are in satisfactory agreement in the neighbourhood of the boiling point of nitrogen.

Strobridge[37], and Ziegler and Mullins[32] analysed the existing thermal and p-V-T data of nitrogen, and deduced also a vapour pressure-temperature relation for liquid nitrogen. They gave the following expressions for the heat capacity of liquid nitrogen at saturation as a function of temperature:

$$C_{\mathrm{L}}\,(\mathrm{J/mole\ ^\circ K}) = 6.246881860\,\frac{T}{(126.26 - T)^2} + 39.39006895 +$$

$$+ 0.6821295539\,T - 0.01052432772T^2 + 6.001046981\,(10^{-5})\,T^3 \qquad (\text{Strobridge}) \quad (4)$$

and

$$C_{\mathrm{L}}\,(\mathrm{cal/mole\ ^\circ K}) = 11.618805 + 0.026456813\,T\ (\mathrm{Z\,\&\,M}). \quad (5)$$

For the present work the data of Clusius, Giauque and Clayton, and Wiebe and Brevoort are considered, to get average values for C_{L} in the temperature range considered (63-85°K). Their average is represented by the following equation:

$$C_{\mathrm{L}}\,(\mathrm{cal/mole\ ^\circ K}) = 11.675 + 0.0267\,T. \quad (6)$$

The values for C_{L} calculated from eqs. (4), (5) and (6) are represented in fig. 1. As can be seen from fig. 1, the values calculated from eqs. (4) and (5) are in good agreement with each other in the region 63-79°K. Both eqs. (4) and (5) are based, in this region, mainly on the data given by Giauque and Clayton. The difference between C_{L} values deduced from our eq. (6) and from eqs. (4) and (5) is mainly due to our choice of C_{L} in which the experimental data of Clusius and of Giauque and Clayton have been given the same weight. The maximum difference between eqs.

(6) and (4) or (5) is about 0.7%. Eq. (6) has been used for the calculation of the terms

$$\int_{T_1}^{T} \Big((C_{V_\text{i}} - C_\text{L})/RT\Big)\,\mathrm{d}T \text{ and}$$

$$(1/RT)\int_{T_1}^{T} \Big(C_{V_\text{i}} - C_\text{L}\Big)\mathrm{d}T\,.$$

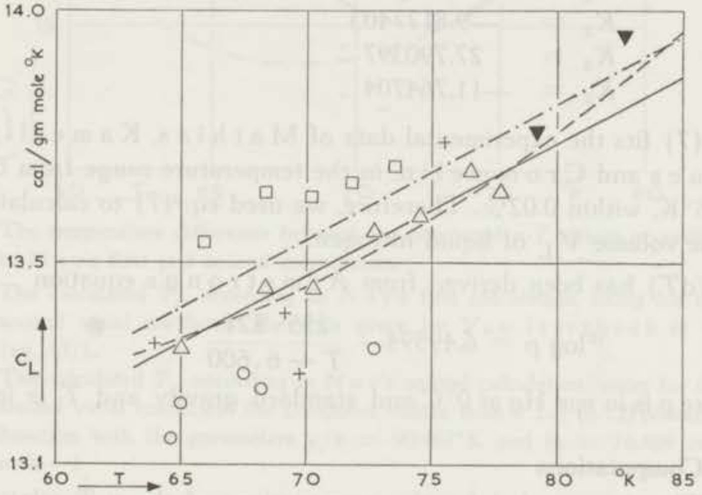

Fig. 1. Heat capacity of liquid nitrogen along the saturation line.

△ Giauque and Clayton
□ Clusius
▼ Wiebe and Brevoort
○ Eucken
\+ Keesom and Kamerlingh Onnes
— — — Strobridge (eq. (4))
——— Ziegler and Mullins (eq. (5))
— · — · — The chosen values for this work and represented by eq. (6)

c. The term $(1/RT)\int_{T_1}^{T} V_\text{L}\,(\mathrm{d}p/\mathrm{d}T)\mathrm{d}T$ contributes only a very small amount to ln p. The density of liquid nitrogen has been measured by Mathias, Kamerlingh Onnes and Crommelin[38] and by Baly and Donnen[39]. The density of saturated liquid nitrogen can be represented by the following equation given by Strobridge:

$$\rho_{\text{sat}}\ (\text{mole/l}) = K_1 + K_2X + K_3X^2 + K_4X^3 + K_5X^4 \qquad (7)$$

where: $X = (1 - \frac{T}{126.26})^{1/3}$

$K_1 = 11.230207$
$K_2 = 21.082073$
$K_3 = -9.8177403$
$K_4 = 27.790397$
$K_5 = -11.764704$.

Eq. (7) fits the experimental data of Mathias, Kamerlingh Onnes and Crommelin, in the temperature range from 63 up to 85°K, within 0.02%. Therefore, we used eq. (7) to calculate the molar volume V_L of liquid nitrogen.

$(\mathrm{d}p/\mathrm{d}T)$ has been derived from Armstrong's equation

$$^{10}\log p = 6.49594 - \frac{255.821}{T - 6.600} \qquad (8)$$

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

4. Computations

a. The data needed for the computations of the p-T relation of liquid nitrogen using eq. (1) or (2) have been collected and discussed in sections 2 and 3 of this chapter. The calculation of the correction terms using the experimental data, and a provisional calculation of $p(T)$ according to eq. (1) were made for us by W. Nuy, assistant at the Mathematical Institute of the University of Leiden. In this provisional calculation $T_1 = 77.3450$°K at $p_1 =$ 760.000 mm Hg at 0°C and standard gravity has been used as reference temperature. Firstly, Nuy did his calculation using for the second virial coefficient the data given by Van Itterbeek et al. and, secondly, those calculated with a Lennard-Jones (6-12) potential function using the parameters, $\varepsilon/k = 90.467$°K and $b_0 =$ 76.869 cm^3 mole^{-1} (the values given by Ziegler and Mullins). The difference between the computed p-T values according to Nuy's first and second calculations, and Armstrong's equation (eq. (8)) are given in fig. 2. The maximum difference that

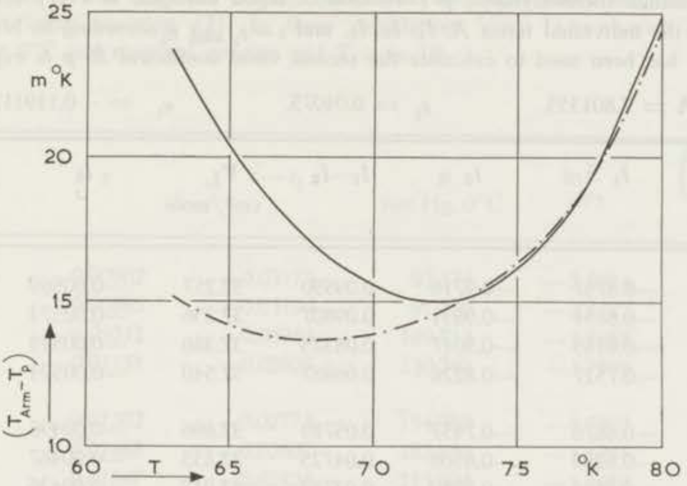

Fig. 2. The temperature difference between the computed p-T values according to Nuy's first and second calculations.

— . — The calculated T_p, according to Nuy's first calculation, using for the second virial coefficient the data given by Van Itterbeek et al. (eq. (3)).

——— The calculated T_p, according to Nuy's second calculation, using for the second virial coefficient the computed values from a L-J (6-12) potential function with the parameters $\varepsilon/k = 90.467°$K and $b_0 = 76.869$ cm^3 mole—1.

occurs between the computed p-T values, according to Nuy's first and second calculations, is 8.5 m°K at 63°K. Nuy did his computation at 25 temperatures from 63 to 85°K and at the boiling point and the triple point. Table I gives the numerical data for the individual terms in eq. (1) according to the first calculation.

b. Because there remained uncertainty in the computed p-T data due to the uncertainties in the different terms in eq. (1) new calculations have been made in a somewhat different way. Again, we started with eq. (2) but instead of calculating the coefficient A from $L(T_1)$ and $\eta(T_1)$, we calculated A using the triple point as a second reference point. For the triple point we chose $p = 93.921$ mm Hg at 0°C, $T = 63.1420$°K (see chapter III, section 8*c*). Moreover, the boiling point was chosen to be 77.3385°K, slightly different from

TABLE I

The provisional thermodynamic p-T relation of liquid nitrogen, at every degree from values of the individual terms A, I_1, I_2, I_3, and $\varepsilon - \varepsilon_1$ and $\varkappa_1$ according to Nuy's first (eq. (3)) has been used to calculate the second virial coefficient B. p is expressed in

$A = 7.801355$, $\varepsilon_1 = 0.04075$, $\varkappa_1 = -0.119117$

T °K	I_1	I_2	I_1—I_2	V_L cm³/mole	I_3	$10^{-3} V_G$ cm³/mole
63.14	—0.8757	—0.9716	0.09590	32.257	—0.00569	41.68
63	—0.8851	—0.9831	0.09807	32.236	—0.00573	42.69
64	—0.8185	—0.9017	0.08323	32.386	—0,00549	36.10
65	—0.7527	—0.8226	0.06987	32.540	—0.00524	30.71
66	—0.6876	—0.7457	0.05789	32.696	—0,00496	26.28
67	—0.6263	—0.6708	0.04725	32.855	—0.00467	22.60
68	—0.5601	—0.5980	0.03785	33.017	—0.00436	19.53
69	—0.4974	—0.5271	0.02964	33.182	—0.00403	16.96
70	—0.4354	—0.4580	0.02255	33.350	—0.00367	14.79
71	—0.3741	—0.3907	0.01653	33.521	—0.00328	12.96
72	—0.3135	—0.3250	0.01153	33.696	—0.00286	11.40
73	—0.2535	—0.2610	0.00749	33.875	—0.00240	10.06
74	—0.1941	—0.1985	0.00436	34.057	—0.00191	8.916
75	—0.1354	—0.1375	0.00211	34.243	—0.00139	7.928
76	—0.0773	—0.0780	0.00068	34.433	—0.00082	7.073
77	—0.0197	—0.0198	0.00004	34.627	—0.00022	6.330
78	0.0373	0.0371	0.00016	34.825	0.00043	5.682
79	0.0937	0.0927	0.00098	35.028	0.00112	5.115
80	0.1496	0.1471	0.00249	35.234	0.00187	4.617
81	0.2049	0.2003	0.00465	35.446	0.00267	4.178
82	0.2598	0.2524	0.00743	35.661	0.00351	3.790
83	0.3141	0.3033	0.01080	35.882	0.00441	3.447
84	0.3680	0.3533	0.01473	36.107	0.00537	3.142
85	0.4214	0.4022	0.01920	36.338	0.00638	2.869
77.345	0.0000	0.0000	0.0000	34.695	0.00000	1.609

* According to Armstrong's equation (eq. 8)).

63 up to 85°K and near the boiling point and the triple point, and the numerical calculation using equation (2). In these calculations Van Itterbeek's equation mm Hg at 0°C and standard gravity and T is in °K.

B/V_G	ε	$\varepsilon-\varepsilon_1$	p mm Hg, 0°C	$\ln\frac{p}{p_1}$	$\left(\frac{d \ln p}{dT}\right)^*$ °K^{-1}
—0.00906	0.00902	—0.03173	93.874	—2.0914	0.1843
—0.00889	0.00885	—0.03190	91.480	—2.1172	0.1852
—0.01017	0.01012	—0.03063	109.713	—1.9355	0.1788
—0.01157	0.01151	—0.02925	130.768	—1.7599	0.1727
—0.01311	0.01302	—0.02773	154.950	—1.5902	0.1669
—0.01479	0.01468	—0.02607	182.580	—1.4261	0.1615
—0.01661	0.01647	—0.02428	213.994	—1.2674	0.1562
—0.01859	0.01841	—0.02234	249.544	—1.1137	0.1513
—0.02072	0.02050	—0.02025	289.596	—0.9648	0.1465
—0.02301	0.02274	—0.01801	334.531	—0.8206	0.1420
—0.02547	0.02514	—0.01561	384.743	—0.6807	0.1377
—0.02811	0.02770	—0.01305	440.638	—0.5451	0.1336
—0.03091	0.03043	—0.01032	502.635	—0.4135	0.1297
—0.03390	0.03332	—0.00744	571.163	—0.2856	0.1259
—0.03708	0.03637	—0.00438	646.664	—0.1615	0.1223
—0.04044	0.03960	—0.00115	729.587	—0.0408	0.1189
—0.04399	0.04300	0.00224	820.391	0.0765	0.1155
—0.04774	0.04656	0.00581	919.545	0.1906	0.1124
—0.05169	0.05031	0.00956	1027.524	0.3016	0.1093
—0.05584	0.05422	0.01347	1144.813	0.4097	0.1064
—0.06020	0.05831	0.01756	1271.900	0.5149	0.1036
—0.06476	0.06257	0.02182	1409.284	0.6175	0.1009
—0.06953	0.06700	0.02625	1557.465	0.7175	0.0983
—0.07452	0.07160	0.03085	1716.953	0.8150	0.0958
—0.04164	0.04075	0.0000	760.000	0.0000	0.1177

the value 77.3450°K chosen in our first calculation. These values for the boiling point and for the triple point temperature and pressure are obtained from our measurements (see chapter III, sections 8*b* and 8*c*). The change of A that we need is only 0.03% and is within the inaccuracy of the available experimental data for $L(T_1)$ and $\varkappa_1$. Instead of doing the complete calculations again, we used the result of Nuy's first calculation (B according to Van Itterbeek's equation).

The coefficient A can be eliminated from eq. (2) if we know the pressures (p_1 and p_2) of the saturated vapour at two temperatures (T_1 and T_2) sufficiently accurately. Eq. (2) can be written:

$$\ln\frac{p}{p_1} = A\left(1-\frac{T_1}{T}\right)+\ln\frac{T}{T_1}+C\,(T,T_1)$$

where $C\,(T,T_1) = I_1\,(T,T_1) - I_2(T,T_1) + {}$
$$+\,I_3\,(T,T_1) + \varepsilon - \varepsilon_1.$$

Quantities as used in Nuy's first calculation are indicated with a subscript N and quantities according to our new calculation without a subscript. It is assumed that $C_{\mathrm{N}}\,(T,T_{1\mathrm{N}})$ is equal to $C(T,T_1)$. This is not strictly right because C depends also on p but, p being always nearly equal to p_{N}, the difference between $C_{\mathrm{N}}(T,T_{1\mathrm{N}})$ and $C(T,T_1)$ can be neglected. Therefore,

$$\frac{T}{T-T_1}\left\{\ln\frac{p_{\mathrm{N}}T_1}{p_{1\mathrm{N}}T}-C(T,T_1)\right\} = \frac{T_2}{T_2-T_1}\left\{\ln\frac{p_{2\mathrm{N}}T_1}{p_{1\mathrm{N}}T_2}-C(T_1,T_2)\right\} \tag{9}$$

and
$$\frac{T}{T-T_1}\left\{\ln\frac{pT_1}{p_1T}-C(T,T_1)\right\} = \frac{T_2}{T_2-T_1}\left\{\ln\frac{p_2T_1}{p_1T_2}-C(T_1,T_2)\right\} = A\,. \tag{10}$$

Substracting eq. (9) from (10) we get:

$$\frac{T}{T-T_1}\left\{\ln\frac{p}{p_1}-\ln\frac{p_{\mathrm{N}}}{p_{1\mathrm{N}}}\right\} = \frac{T_2}{T_2-T_1}\left\{\ln\frac{p_2}{p_1}-\ln\frac{p_{2\mathrm{N}}}{p_{1\mathrm{N}}}\right\} \tag{11}$$

and
$$\ln\frac{p}{p_{\mathrm{N}}}-\ln\frac{p_1}{p_{1\mathrm{N}}} = \left(\ln\frac{p_2}{p_{2\mathrm{N}}}-\ln\frac{p_1}{p_{1\mathrm{N}}}\right)\frac{T_2}{T_2-T_1}\left(1-\frac{T_1}{T}\right). \tag{12}$$

where p_{1N} is 760.000 mm Hg at 0°C and standard gravity at 77.345°K, the temperature which has been taken for the reference temperature T_1 in the first calculation of Nuy (table I).

p_{2N} is 93.874 mm Hg at 0°C and standard gravity which corresponds to T_2 = 63.1400°K according to Nuy's first computation (see table I).

p_N is the computed pressure as a function of temperature according to Nuy's first calculation. 25 values of T and p are given in table I. p is the final pressure as a function of temperature calculated with the new values of p_1 and p_2. The result of the calculation is given in table II. The new values are p_1 = 760.580 mm Hg, 0°C at 77.345°K, and p_2 = 93.8865 mm Hg, 0°C at 63.140°K corresponding to a pressure of 760.000 mm Hg, 0°C at 77.3385°K and to a pressure of 93.921 mm Hg, 0°C at 63.1420°K, as dp/dT at 77.345°K and 63.1400°K is 89.2489 and 17.2499 mm Hg, 0°C/°K respectively. It is clear that the differences between p_{1N} (760.000) and p_1 (760.580), and p_{2N} (93.874) and p_2 (93.8865) are very small. Therefore, $\ln \frac{p}{p_N}$ can be written:

$$\ln \frac{p}{p_N} = \ln\left(1+\frac{p-p_N}{p_N}\right) \approx \frac{p-p_N}{p_N} = \frac{p}{p_N} - 1 \tag{13}$$

and eq. (12) can be written:

$$\frac{p}{p_N} = \frac{p_1}{p_{1N}} + \left(\frac{p_1}{p_{1N}} - \frac{p_2}{p_{2N}}\right)\frac{T_2}{T_1 - T_2}\left(1-\frac{T_1}{T}\right).$$

Then,

$$p = p_N\left\{\frac{p_1}{p_{1N}} + \left(\frac{p_1}{p_{1N}} - \frac{p_2}{p_{2N}}\right)\frac{T_2}{T_1 - T_2}\left(1-\frac{T_1}{T}\right)\right\} \tag{14}$$

and

$$p - p_N = p_N\left\{\frac{p_1 - p_{1N}}{p_{1N}} + \left(\frac{p_1 - p_{1N}}{p_{1N}} + \right.\right.$$

$$\left.\left. + \frac{p_{2N} - p_2}{p_{2N}}\right)\frac{T_2}{T_1 - T_2}\left(1-\frac{T_1}{T}\right)\right\} = \Delta p. \tag{15}$$

Therefore using eq. (15) we get:

$$p - p_{\mathrm{N}} = p_{\mathrm{N}} \left\{ \frac{0.580}{760.000} + \right.$$

$$\left. + \left(\frac{0.580}{760.000} - \frac{0.0125}{93.874} \right) \frac{63.1400}{77.345 - 63.1400} \left(1 - \frac{77.345}{T} \right) \right\}$$

and $p = p_{\mathrm{N}} +$

$$+ p_{\mathrm{N}} \left\{ 0.00076316 + 0.00280029 \quad \left(1 - \frac{77.345}{T} \right) \right\} \qquad (16)$$

where p_{N} is the pressure values given by Nuy in his first computation (see table I) and

p is the corresponding pressure according to the new calculation at the same temperature. Our finally computed 25 p-T values were deduced from Nuy's first computation (see table I), using eq. (16). The difference between the results of our new calculation and of Nuy's first calculation can be given in a simple formula:

$$p - p_{\mathrm{N}} = p_{\mathrm{N}} \left\{ 0.00076316 + 0.00280029 \left(1 - \frac{77.345}{T} \right) \right\}. \qquad (16')$$

Finally p was calculated at one tenth of a degree intervals from 63 up to 85°K using the following equation:

$${}^{10}\log p \text{ (mm Hg, 0°C)} = C_0 + C_1 T + C_2 T^2 + C_3 \, {}^{10}\log T +$$

$$+ \frac{C_4}{T} + \frac{C_5}{T^2} + \frac{C_6}{T^3} \qquad (17)$$

where: $C_0 = -.563682443701 \times 10^3$
$C_1 = -.840179813594 \times 10$
$C_2 = +.116453083780 \times 10^{-2}$
$C_3 = +.283349281469 \times 10^{+3}$
$C_4 = +.886507583526 \times 10^{+4}$
$C_5 = -.172276651422 \times 10^{+6}$
$C_6 = +.170065634641 \times 10^{+7}$.

The seven coefficients in eq. (17) were deduced by using seven p-T values calculated from eq. (16) and table I. The seven p-T values include the boiling point (77.3385°K at 760.000 mm Hg, 0°C) and

TABLE II

The vapour pressure-temperature relation of liquid nitrogen according to the thermodynamic relation (equation (1)) and computed with equation (17). p is expressed in mm Hg 0°C and standard gravity.

T°K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
63	91.492	93.197	94.928	96.685	98.468	100.277	102.114	103.977	105.868	107.786
64	109.732	111.707	113.710	115.742	117.803	119.893	122.013	124.164	126.344	128.556
65	130.798	133.071	135.377	137.714	140.083	142.485	144.920	147.388	149.889	152.424
66	154.994	157.598	160.236	162.910	165.620	168.365	171.146	173.964	176.819	179.711
67	182.640	185.608	188.613	191.657	194.740	197.863	201.024	204.226	207.468	210.751
68	214.075	217.440	220.847	224.296	227.788	231.322	234.900	238.521	242.186	245.896
69	249.650	253.449	257.294	261.184	265.121	269.104	273.134	277.212	281.337	285.510
70	289.732	294.003	298.322	302.692	307.112	311.582	316.103	320.675	325.299	329.974
71	334.702	339.483	344.318	349.206	354.147	359.144	364.195	369.301	374.463	379.682
72	384.956	390.288	395.677	401.123	406.628	412.191	417.813	423.495	429.237	435.038
73	440.901	446.824	452.809	458.856	464.965	471.137	477.373	483.672	490.035	496.462
74	502.955	509.513	516.137	522.827	529.584	536.408	543.299	550.259	557.287	564.384
75	571.550	578.786	586.093	593.470	600.918	608.438	616.030	623.694	631.431	639.242
76	647.127	655.086	663.120	671.228	679.413	687.674	696.011	704.426	712.918	721.488
77	730.136	738.864	747.671	756.557	765.524	774.572	783.701	792.912	802.205	811.580
78	821.039	830.581	840.208	849.919	859.715	869.596	879.564	889.618	899.759	909.987
79	920.303	930.708	941.201	951.784	962.457	973.220	984.073	995.018	1006.055	1017.184
80	1028.406	1039.721	1051.129	1062.632	1074.230	1085.923	1097.711	1109.596	1121.577	1133.655
81	1145.831	1158.105	1170.478	1182.950	1195.522	1208.193	1220.966	1233.839	1246.814	1259.891
82	1273.071	1286.354	1299.740	1313.231	1326.826	1340.527	1354.333	1368.245	1382.264	1396.390
83	1410.624	1424.966	1439.416	1453.976	1468.645	1483.425	1498.315	1513.317	1528.431	1543.656
84	1558.995	1574.446	1590.012	1605.692	1621.487	1637.397	1653.423	1669.565	1685.825	1702.202
85	1718.696	1735.310	1752.042	1768.894	1785.866	1802.958	1820.172	1837.507	1854.964	1872.545

TABLE III

The derivative dp/dT according to the thermodynamic p-T relation of liquid nitrogen (eq. (1)) and computed with equation (17). dp/dT is expressed in mm Hg at 0°C/°K as a function of T in °K at every tenth of a degree.

T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
63	16.9248	17.1798	17.4377	17.6983	17.9619	18.2282	18.4975	18.7696	19.0447	19.3227
64	19.6036	19.8875	20.1744	20.4643	20.7571	21.0531	21.3520	21.6540	21.9591	22.2673
65	22.5786	22.8931	23.2106	23.5314	23.8553	24.1824	24.5127	24.8463	25.1831	25.5231
66	25.8664	26.2130	26.5630	26.9162	27.2728	27.6327	27.9960	28.3627	28.7328	29.1063
67	29.4832	29.8636	30.2475	30.6348	31.0256	31.4199	31.8178	32.2192	32.6241	33.0326
68	33.4447	33.8604	34.2797	34.7027	35.1293	35.5595	35.9934	36.4310	36.8723	37.3173
69	37.7660	38.2185	38.6748	39.1348	39.5986	40.0662	40.5376	41.0128	41.4919	41.9748
70	42.4616	42.9523	43.4469	43.9454	44.4478	44.9541	45.4644	45.9787	46.4969	47.0191
71	47.5453	48.0755	48.6098	49.1481	49.6904	50.2368	50.7827	51.3418	51.9005	52.4633
72	53.0302	53.6012	54.1764	54.7557	55.3392	55.9269	56.5188	57.1149	57.7152	58.3197
73	58.9285	59.5416	60.1588	60.7804	61.4063	62.0364	62.6709	63.3097	63.9528	64.6002
74	65.2520	65.9082	66.5687	67.2336	67.9029	68.5766	69.2547	69.9373	70.6243	71.3157
75	72.0115	72.7119	73.4167	74.1260	74.8397	75.5580	76.2808	77.0081	77.7400	78.4763
76	79.2173	79.9627	80.7128	81.4674	82.2266	82.9904	83.7588	84.5318	85.3095	86.0918
77	86.8787	87.6702	88.4664	89.2673	90.0728	90.8830	91.6979	92.5175	93.3418	94.1708
78	95.0046	95.8431	96.6863	97.5342	98.3867	99.2444	100.1066	100.9736	101.8454	102.7220
79	103.6033	104.4895	105.3805	106.2763	107.1770	108.0825	108.9928	109.9080	110.8280	111.7529
80	112.6827	113.6174	114.5569	115.5014	116.4507	117.4050	118.3641	119.3282	120.2972	121.2712
81	122.2501	123.2339	124.2228	125.2165	126.2153	127.2190	128.2277	129.2414	130.2601	131.2838
82	132.3126	133.3463	134.3851	135.4289	136.4777	137.5316	138.5905	139.6546	140.7236	141.7978
83	142.8770	143.9613	145.0507	146.1453	147.2449	148.3496	149.4595	150.5745	151.6946	152.8199
84	153.9503	155.0859	156.2266	157.3726	158.5237	159.6800	160.8414	162.0081	163.1800	164.3571
85	165.5394	166.7270	167.9198	169.1178	170.3211	171.5297	172.7435	173.9626	175.1869	176.4166

TABLE IV

The values of the pressure p computed using our thermodynamic equation (1) (table II), Armstrong's equation (eq. (8)) and those given by Ziegler and Mullins, and the differences $T_{\mathrm{Arm.}} - T_p$ and $T_{\mathrm{Z\&M}} - T_p$.

T °K	$p_{\mathrm{ther.}}$ table II mm Hg, 0°C	$p_{\mathrm{Arm.}}$ eq. (8) mm Hg, 0°C	$p_{\mathrm{Z\&M}}$ mm Hg, 0°C	$(\mathrm{d}p/\mathrm{d}T)$* mm Hg, 0°C/°K	$(T_{\mathrm{Arm.}} - T_p)$ m°K	$T_{\mathrm{Z\&M}} - T_p$ m°K
63	91.492	91.223	—	16.8927	15.9	—
64	109.732	109.428	109.742	19.5639	15.5	—0.5
65	130.798	130.450	130.785	22.5304	15.4	0.6
66	154.994	154.593	154.952	25.8088	15.5	1.6
67	182.640	182.177	182.563	29.4151	15.7	2.6
68	214.075	213.938	213.956	33.3649	16.1	3.6
69	249.650	249.026	249.482	37.6727	16.6	4.5
70	289.732	289.007	289.508	42.3528	17.1	5.3
71	334.702	333.860	334.420	47.4181	17.8	5.9
72	384.956	383.976	384.607	52.8811	18.5	6.6
73	440.901	439.758	440.479	58.7530	19.5	7.2
74	502.955	501.622	502.456	65.0442	20.5	7.7
75	571.550	569.990	570.972	71.7640	21.7	8.1
76	647.127	645.295	646.468	78.9208	23.2	8.4
77	730.136	727.979	729.398	86.5218	24.9	8.5
78	821.039	818.489	—	94.5732	27.0	—

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* According to Armstrong's equation.

the triple point temperature and pressure (63.1420°K and 93.921 mm Hg, 0°C). Eq. (17) gives the pressure p in mm Hg, 0°C as a function of T in °K. It represents the 25 p and T values computed from eq. (16) with a maximum deviation of only 0.03 m°K. The computed p-T values and their first derivatives $\mathrm{d}p/\mathrm{d}T$ according to eq. (17) are given in tables II and III respectively. These tables give the pressure p and also $\mathrm{d}p/\mathrm{d}T$ as functions of temperature at every tenth of a degree from 63 to 85°K. These temperatures are denoted by T_p. The temperatures corresponding to our measured pressures (see chapter III) were obtained from table II.

5. Discussion of the results

Our thermodynamically calculated values for p using eq. (1), the p values according to Armstrong (eq. (8)) and those given by Ziegler and Mullins as a result of their thermodynamic calculation, are given in table IV as functions of T. From pressure differences the corresponding temperature differences have been calculated using $\mathrm{d}p/\mathrm{d}T$ values derived from eq. (8).

The deviations $(T_\mathrm{Arm.} - T_\mathrm{p})$ and $(T_{\mathrm{Z\,\&\,M}} - T_\mathrm{p})$ versus T were

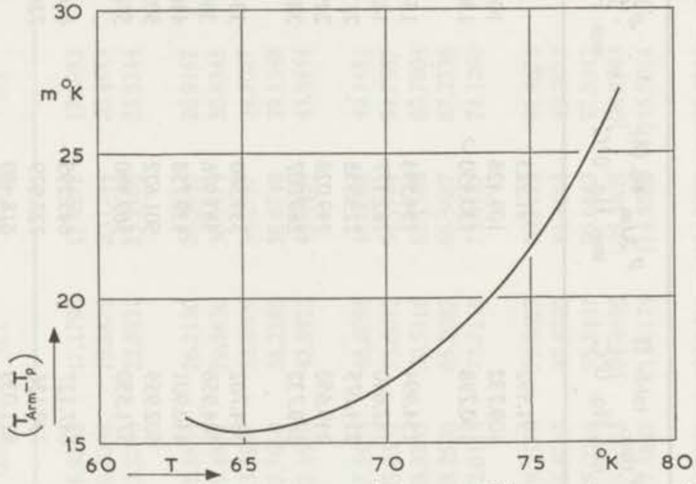

Fig. 3. Temperature differences between $T_\mathrm{Arm.}$ and T_p according to table IV. T_p is the temperature according to our final thermodynamic p-T relation given in table II.

plotted in figs. 3 and 4 respectively. It is clear, as can be seen from table IV and fig. 3, that the differences between our temperature, T_p and $T_{Arm.}$ are comparatively large. The main reason for this is that Armstrong used the NBS-1939 temperature scale, while we used the CCT-64 scale.

The difference between the results of our thermodynamic calculation and the results of Ziegler and Mullins thermodynamic calculation is nowhere larger than about 8.5 m°K. This largest difference occurs near the boiling point. This is due to the choice of Ziegler and Mullins for the temperature at the boiling point (77.347°K). They used this value in their thermodynamic calculations as a reference temperature. Their value 77.347°K is on a thermodynamic scale on which the boiling point of oxygen is 90.168°K. Anyhow it is satisfactory that the difference between the results from both thermodynamic calculations is so small.

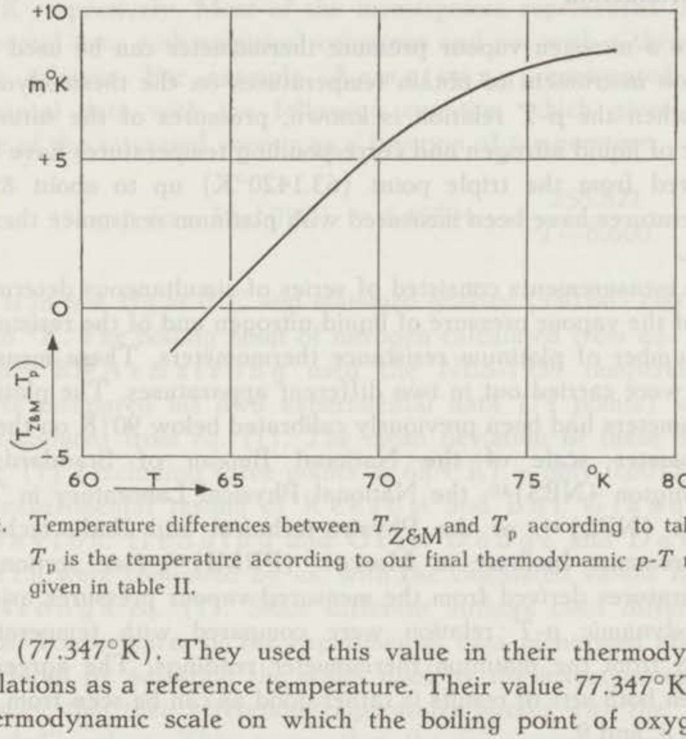

Fig. 4. Temperature differences between $T_{Z\&M}$ and T_p according to table IV. T_p is the temperature according to our final thermodynamic p-T relation given in table II.

CHAPTER III

MEASUREMENTS OF THE VAPOUR PRESSURE-TEMPERATURE RELATION OF LIQUID NITROGEN

1. Introduction

Since a nitrogen vapour pressure thermometer can be used as a precision instrument to obtain temperatures on the thermodynamic scale when the *p-T* relation is known, pressures of the saturated vapour of liquid nitrogen and corresponding temperatures have been measured from the triple point (63.1420°K) up to about 85°K. Temperatures have been measured with platinum resistance thermometers.

The measurements consisted of series of simultaneous determinations of the vapour pressure of liquid nitrogen and of the resistances of a number of platinum resistance thermometers. These measurements were carried out in two different apparatuses. The platinum thermometers had been previously calibrated below 90°K on the gas thermometer scale of the National Bureau of Standards in Washington (NBS)[40], the National Physical Laboratory in Teddington (NPL)[41], or the Physico-technical and Radio-technical Measurements Institute in Moscow (PRMI)[42] (see section 7). Temperatures derived from the measured vapour pressures using a thermodynamic *p-T* relation were compared with temperatures derived from the platinum thermometer readings. The agreement between both sets of results is rather good as can be seen from figs. 5, 6, 7, 8, and 9.

According to our measurements the boiling point and the triple point temperatures of liquid nitrogen are 77.3385°K and 63.1420°K respectively, on the CCT-64 scale[43] (see section 2), and the triple point pressure is 93.921 mm Hg at 0°C and standard gravity (980.665 cm/s^2).

2. Review of the published experimental data

The vapour pressure-temperature relation of liquid nitrogen has been measured by Crommelin[44], Cath[45], Porter and Berray[46], Dodge and Davis[47], Giauque and Clayton[20], Keesom and Bijl[48], Henning and Otto[49], Hoge and King[50], Michels, Wassenaar, De Graaff and Prins[51], Armstrong[33], and Friedman and White[52]. Strobridge, and Ziegler and Mullins deduced thermodynamic p-T relations for liquid nitrogen and computed the p-T values of nitrogen in the range of 64 up to 126°K and 10 to 77.347°K respectively. Most of the investigators represented their experimental data with empirical equations and not with a thermodynamic relation. For example, Armstrong represented his experimental data with the following equation which gives the pressure of the saturated vapour as a function of temperature,

$$^{10}\log p \text{ (mm Hg, 0°C)} = 6.49594 - \frac{255.821}{T - 6.600} . \quad (1)$$

Here p is in mm Hg at 0°C and standard gravity (980.665 cm/s^2) and T in °K. The boiling point of nitrogen calculated from eq. (1) is 77.3639°K. Armstrong used the NBS-1939 temperature scale. He compared his own experimental data (74 points) with values computed from eq. (1). The mean deviation of these data from eq. (1) (excluding three points at 68.4°K) is only 0.0012°K.

The experimental results of Keesom and Bijl, Giauque and Clayton, Henning and Otto, Dodge and Davis and Cath were compared by us, with the calculated values from Armstrong's eq. (1). Since different authors used different scales, all temperatures of the experimental data mentioned above were reduced by adjusting the scales used by the investigators in such a way, that their reference temperatures agrees with the "recommended" values. This means that the ice point temperature becomes 273.15°K and the temperature of the normal boiling point of oxygen becomes 90.168°K, the value recommended by Van Dijk[53] in 1958, see the appendix, paragraphs 1 and 2 in reference 54. The reduced temperatures were compared with those calculated from Armstrong's equation, corrected to 90.168°K for the oxygen boiling point (see the appendix, paragraph 2 in reference 54). Fig. 1 shows the deviation $(T_{\text{obs. corr.}} - T_{\text{Armstrong corr.}})$, where $T_{\text{obs. corr.}}$ is the reported temperature corrected, where possible, to an ice point of 273.15°K or to the oxygen point of 90.168°K, and corresponding to the experimentally determined pressure. $T_{\text{Armstrong corr.}}$ is the temperature, corresponding to the same

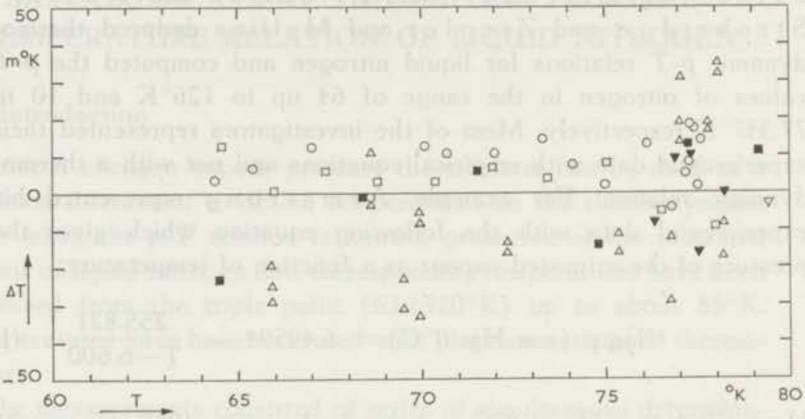

Fig. 1. Temperature differences $\triangle T = T_{\text{obs. corr.}} - T_{\text{Arm. corr.}}$ for the published experimental p-T data for liquid nitrogen.

○ Keesom and Bijl
△ Henning and Otto
□ Giauque and Clayton
▼ Dodge and Davis
■ Cath

pressure, but calculated uing eq. (1) and corrected to the normal boiling point of oxygen 90.168°K. The agreement of the reduced results of Giauque and Clayton and of Keesom and Bijl with the reduced data of Armstrong as calculated from eq. (1) is satisfactory. The differences are 0.003 ± 0.011°K (where 0.003°K is the average deviation and 0.011°K is the maximum deviation from the average) and 0.010 ± 0.008°K respectively. It can be seen from fig. 1 that the experimental data of Giauque and Clayton and of Keesom and Bijl are consistent with each other and with Armstrong's equation. The agreement with the result of Dodge and Davis especially in the region from 76 to

79°K is not bad. Its deviation from Armstrong's equation is —0.001 ± 0.014°K. The agreement with the data of Cath, and of Henning and Otto is not as good. The experimental data of Cath deviate in a systematic way and those of Henning and Otto scatter over a wide range. Their deviations are 0.004 ± 0.025°K and —0.005 ± 0.035°K respectively.

The experimental results of Armstrong were compared by Ziegler and Mullins with their own computed p-T values. The agreement was satisfactory. Both results agreed within 0.005°K when reduced to the same oxygen point. According to this discussion it appears that Armstrong's eq. (1) is rather good. We used it for computing a provisional table for the p-T relation of liquid nitrogen from the triple point to the boiling point.

3. General description of the apparatus

Two different apparatuses A and B were used for the measurements of the vapour pressure-temperature relation of liquid nitrogen. In both, the platinum resistance thermometers were placed in a copper block. The two apparatuses are shown in detail in fig. 2.

a. Apparatus A

A sketch of apparatus A is shown in fig. 2*a*. This apparatus was used for the measurements from 7th Nov. 1963 to 12th Jan. 1964. The low temperature part of apparatus A consisted of a vessel C_1 made of German silver (G.S.) in which liquid nitrogen was condensed, and in which a copper block C was suspended. C_1 forms the reservoir Th of the vapour pressure thermometer. The vessel C_1 was surrounded by another can C_2 made of brass. C_2 could be evacuated or filled with nitrogen gas for heat transfer. The copper block C contained four similar holes in which the platinum resistance thermometers were placed. These holes were open at the bottom of the copper block, to allow the condensed liquid to enter into the holes, to ensure the thermal equilibrium between the thermometers and the condensed liquid. Since the dimensions of the platinum thermometers which we used were not the same, we filled the holes partly with copper to bring the centre of all the platinum thermo-

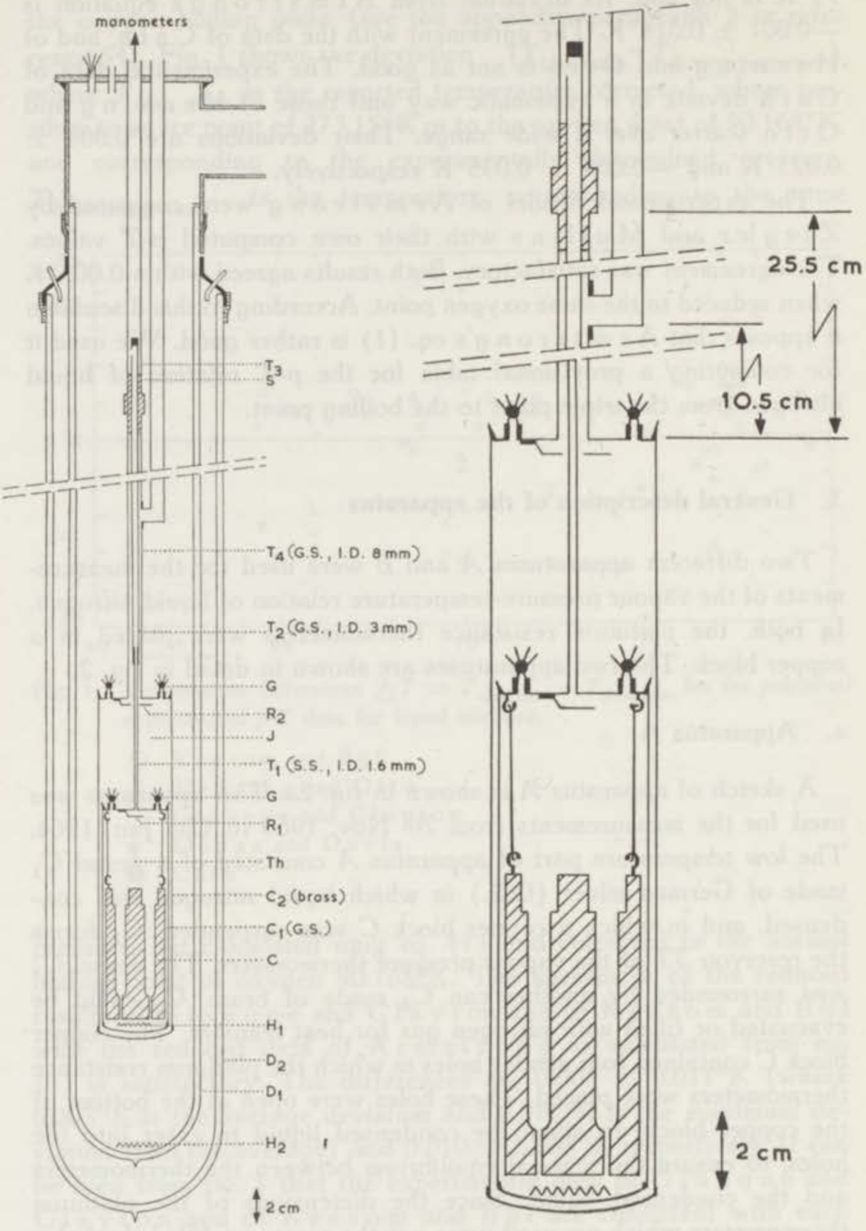

Fig. 2*a*. Apparatus for vapour pressure and temperature measurements between the triple point and the boiling point of liquid nitrogen.

meters at the same horizontal plane so that the temperatures of the four thermometers were accurately equal. The temperature gradient in the block C was practically zero. This became evident from measurements with different amounts of liquid in the inner vessel Th. The liquid level has to be a little below the upper surface of the block. Under the copper block there was a heater H_1. It consisted of a mica plate, around which a constantan wire of about 35 Ω was wound.

The lower end of the tube connecting the manometer system to the inner vessel Th was a stainless steel capillary tube (T_1) of small diameter (inner diameter 1.6 mm and outer diameter 2 mm). It allows only a very small heat influx into Th. The lower part of the tube T_1 was double walled in order to prevent condensation of the gas in the tube. It had a radiation shield R_1 to reduce the heat input into the equilibrium vessel Th by radiation. At its top T_1 was soldered to a wider tube T_2 (made of German silver and of inner diameter of 3 mm). The tube T_2 was not leading directly outside the cryostat, but it was connected to a wider tube T_3 at the junction S which was at 255 mm above the top of the outer can C_2. The upper end of the tube T_2 was closed at its top but open aside to reduce the heat input by radiation.

The outer tube T_4 (made of German silver and of inner diameter of 8 mm) surrounded the central tube and connected the can C_2 with the gas filling system, the Mcleod gauge, and the pumping system. T_4 has been extended by a side tube (see fig. 2*a*) to reduce the heat input by radiation. At the lower end of T_4 there was a radiation shield R_2. The inner can C_1 and the outer can C_2 had, at their tops, three platinum-to-glass seals, G. Each of the seals had four platinum wires for bringing the leads, of the platinum thermometers and those of the heater, to the outside of both cans.

The whole assembly was mounted in a silvered dewar D_1 with two unsilvered slits of about 7 mm at opposite sides. The dewar was filled with liquid nitrogen. The temperature of this nitrogen bath can be kept constant at a temperature nearly equal to the temperature of the inner can. The cans were immersed completely in the constant-temperature nitrogen bath. The nitrogen bath was surrounded by a second dewar D_2 filled with liquid nitrogen boiling at atmospheric pressure. During the measurements, the nitrogen level in D_1 was kept below the junction S to avoid condensation in the tube T_3.

In the vessel Th, we condensed about 8 cm^3 of very pure liquid nitrogen (see section 5e) of which the vapour pressure could be measured. The block was partly immersed in the condensed nitrogen during the measurements. We have checked the effect of the amount of the condensed liquid nitrogen on the results but found no difference within the limits of our accuracy. The heat contact between the constant-temperature nitrogen bath and the copper block can be changed by modifying the pressure of the nitrogen gas in the jacket J (between the walls of the inner and outer cans C_1 and C_2). Usually we used a pressure of about 10^{-2} mm Hg in the jacket J. In the vessel Th, equilibrium condition could be realized to a satisfactory degree. This apparatus A was used for the vapour pressure and temperature measurements from the boiling point of nitrogen down to the triple point and at the triple point.

b. Apparatus *B*

A sketch of apparatus B is shown in fig. 2*b*. Apparatus B was used from 8th June 1964 to 25th Sept. 1964 for measurements from about 63.5 up to 84.5°K. The low temperature part of apparatus B consisted of a copper block with a cavity in the centre serving as the reservoir of a vapour pressure thermometer Th and eight similar holes in which the capsule-type platinum resistance thermometers could be placed. The copper block C was surrounded by two copper shields a and b fastened around the block near its top with small screws. The lower shield a surrounded the lower part of the block, that contained the platinum thermometers and the vapour pressure thermometer reservoir Th. The upper shield b covered the connections of the leads with the platinum thermometers, to reduce thermal EMF's due to temperature differences between soldered connections in the leads. This shield b was cut into two halves to facilitate the assembling.

The shield a was not entirely closed but contained four small holes. three of them were at equal distance from each other near the top while the fourth was at the centre of its bottom. The space between the shield a and the copper block was only 1 mm. The main

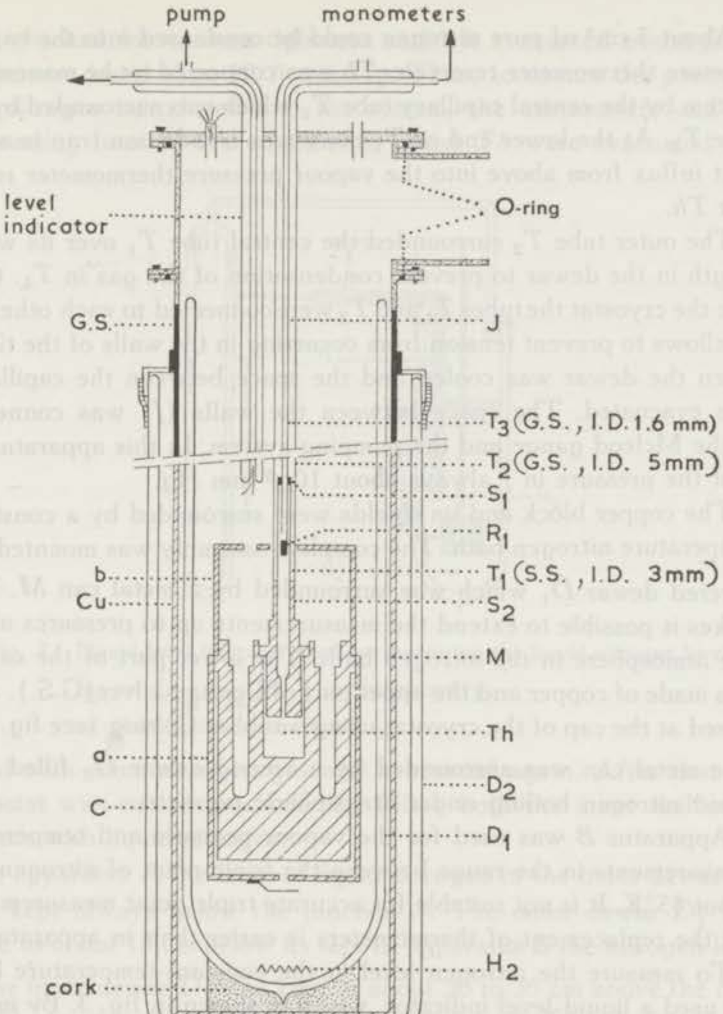

Fig. *2b.* Apparatus for vapour pressure and temperature measurements from the triple point of nitrogen up to pressures above one atmosphere in the nitrogen bath.

purpose of the shield *a* is to reduce the vertical temperature gradient which might occur due to the temperature gradient caused by the hydrostatic pressure gradient in the bath.

About 3 cm^3 of pure nitrogen could be condensed into the vapour pressure thermometer reservoir. *Th* was connected tot he manometer system by the central capillary tube T_1 which was surrounded by the tube T_2. At the lower end of T_1 there was a radiation trap to avoid heat influx from above into the vapour pressure thermometer reservoir *Th*.

The outer tube T_2 surrounded the central tube T_1 over its whole length in the dewar to prevent condensation of the gas in T_1. Outside the cryostat the tubes T_1 and T_2 were connected to each other via a bellows to prevent tension from occurring in the walls of the tubes, when the dewar was cooled and the space between the capillaries was evacuated. The space between the walls (*J*) was connected to the Mcleod gauge and the pumping system. In this apparatus we kept the pressure in *J* always about 10^{-5} mm Hg.

The copper block and its shields were surrounded by a constant-temperature nitrogen bath. The complete assembly was mounted in a silvered dewar D_1 which was surrounded by a metal can *M*. This makes it possible to extend the measurements up to pressures above one atmosphere in the nitrogen bath. The lower part of the can *M* was made of copper and the upper part of German silver (G.S.). *M* is closed at the cap of the cryostat using a rubber O -ring (see fig. 2*b*). The metal can was surrounded by a second dewar D_2 filled with liquid nitrogen boiling under atmospheric pressure.

Apparatus *B* was used for the vapour pressure and temperature measurements in the range between the triple point of nitrogen and about 85°K. It is not suitable for accurate triple point measurements, but the replacement of thermometers is easier than in apparatus *A*.

To measure the nitrogen level in the constant-temperature bath, we used a liquid-level indicator, which is shown in fig. 3. By means of a heating element H_3 the liquid is driven out of the tube T_1. The oil differential manometer *m* indicates the difference between the pressure in T_1 and the pressure above the nitrogen bath. This pressure difference corresponds to the weight of the liquid nitrogen column h_2. T_1 is surrounded over its whole length in the nitrogen bath by a vacuum jacket.

4. Procedure of measurements

Before starting measurements, the vapour pressure thermometer was checked for vacuum-tightness and left evacuated overnight at a pressure lower than 10^{-5} mm Hg. Then, to ensure the purity of the nitrogen introduced into the system, the manometers and the connecting lines to the equilibrium vessel *Th* were evacuated and

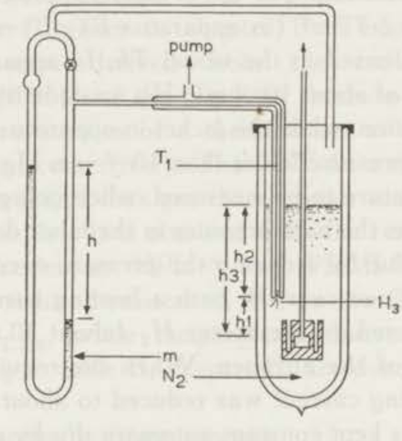

Fig. 3. Liquid-level indicator used for measuring the liquid nitrogen level.
$h_2 = (\rho_{oil}/\rho_{N_2})h$, ρ is the density
m oil differential manometer.

filled with some nitrogen gas and evacuated again. After that the cryostat was cooled gradually by filling both the inner and outer dewars with liquid nitrogen.

In apparatus *A* the level of liquid nitrogen in the inner dewar D_1 was kept always below the junction *S*. The outer dewar D_2 was filled to about 10 cm below its top. In apparatus *B* the nitrogen level in the inner dewar D_1 was kept at about 30 to 35 cm above the copper block using the liquid-level indicator described in paragraph 3*b*. The outer dewar D_2 was filled during the measurements below the boiling point of nitrogen to about 10 cm from its top. During measurements above the boiling point of nitrogen, the liquid level in the outer dewar D_2 was kept below the bottom of the metal tube *M* to avoid condensation of nitrogen gas between the walls of D_1 and *M* which might disturb the equilibrium in the constant-temperature bath in D_1. Usually, the liquid nitrogen in the outer dewars was boiling freely at the atmospheric pressure. The main purpose of the secondary liquid-nitrogen bath, D_2 or $\grave{D}_2$, was to reduce the effects of radiation and losses of liquid nitrogen from the constant-temperature nitrogen bath, in D_1 and $\grave{D}_1$, and thus permitting a longer operation before refilling is required.

After cooling and filling of the cryostat, approximately 8 cm^3 (in apparatus A) or 2-3 cm^3 (in apparatus B) of very pure liquid nitrogen were condensed in the vessel Th. In apparatus A, nitrogen gas at a pressure of about 10^{-2} mm Hg was admitted into the jacket J for heat conduction, while the jacket in apparatus B was evacuated and always at a pressure lower than 10^{-5} mm Hg.

At any temperature to be measured, when going from a higher to lower temperature, the bath pressure in the inner dewar was brought to the desired value by reducing the pressure over the bath. When reducing the pressure over the bath a heating current of about 200 to 500 mA was used, in the heater H_2 (about 40 Ω), to avoid too vigorous boiling of the nitrogen. When the required pressure was reached the heating current was reduced to about 100 mA and the bath pressure was kept constant automatically by a cartesian manostat. At lower pressures, where the manostat was less sensitive, the cryostat pressure was kept constant manually by controlling the valves in the reducing line. Pressure adjustments could be made easily by observing a mercury manometer (for rough indication) and an oil differential manometer with a constant reference pressure (for fine adjustment), which were connected with the constant-temperature nitrogen bath. Keeping the bath pressure contant, temperature equilibrium in D_1 or $\grave{D}_1$, was reached after about 30 minutes. After reaching equilibrium a series of simultaneous readings of the resistance of the platinum thermometers and of the pressure of the saturated vapour of the condensed liquid nitrogen in the reservoir Th were made during 30 to 40 minutes. The observed temperature drifts were of the order 0.010 ± 0.005°K in 30 minutes.

The measurements were made going from lower to higher temperatures and also from higher to lower temperatures to check the reproducibility of the measurements. When going from lower to higher temperature the valves in the reducing line or the evaporating line were closed and the heater current was switched on. A heating current of 200 to 500 mA was used. When the bath pressure had reached the desired value the heating current was reduced to about

100 mA and then the bath pressure was kept constant automatically or manually. Keeping the bath pressure constant, after about 30 minutes temperature equilibrium in the constant-temperature nitrogen bath, D_1 or $\grave{D}_1$, was reached.

Temperatures were derived from the measured vapour pressures using table II given in chapter II. Temperatures on the CCT-64 scale were derived from the reduced resistances ($W = R(T)/R(0°\mathrm{C})$) of the platinum thermometers. $R(T)$ and $R(0°\mathrm{C})$ are the resistances of a thermometer at a temperature T and at the ice point respectively. The CTT-64 scale (see III 7*b*-2) is a smoothed average of four gas thermometer scales (NBS, PSU, NPL and PRMI scale). It is obtained from the results of the intercomparisons of scales at NPL[55] and PRMI[56]. Temperatures derived from the reduced resistance, W, on the CCT-64 scale are denoted by $T_{\mathrm{CCT\text{-}64}}$, while temperatures derived from pressure readings according to table II, chapter II, are denoted by T_{p}.

5. The vapour pressure measurements

The most essential parts of the equipment for measuring the pressure of the saturated vapour of liquid nitrogen, in the considered temperature range, are the vapour pressure thermometer and the mercury manometers.

a. The vapour pressure thermometer

The vapour pressure thermometer consisted of the reservoir *Th*, which was connected to the mercury manometers, and the jacket *J* surrounding the capillary tube T_1 (fig. 2*a*). T_1 was chosen narrow and provided with radiation shields to reduce the heat input into *Th* by radiation and by heat conduction along the tube. T_1 was surrounded by a jacket to prevent condensation of the gas in the capillary tube due to a temperature gradient in the bath.

To obtain accurate results for the temperature dependence of the saturated vapour of a condensed gas, liquid and vapour in the reservoir *Th* have to be in thermal equilibrium with each other, with the copper block and with the platinum thermometers in the block.

b. Manometers

In the considered temperature region (63.1420 to 84.5°K) the pressures to be measured ranged between 93.921 and about 1630 mm Hg at 0°C. For the range from 93.921 to about 820 mm Hg a normal mercury manometer with an inner diameter of about 28 mm was used. One side of the manometer was connected to the vapour pressure thermometer reservoir *Th* while the other side was connected to the vacuum pump. The manometer was placed in an aluminium enclosure to keep its temperature uniform.

For pressures from 820 to 1630 mm Hg two separate mercury manometers were used. These two manometers were similar to the one mentioned above. The first manometer was connected at one side to the vapour pressure thermometer reservoir *Th* while the other side was open to the atmosphere, see fig. 4. The second manometer was used to read the atmospheric pressure accurately, one side of the manometer was open to the atmosphere while the other side was connected to the pumping system during the measurements.

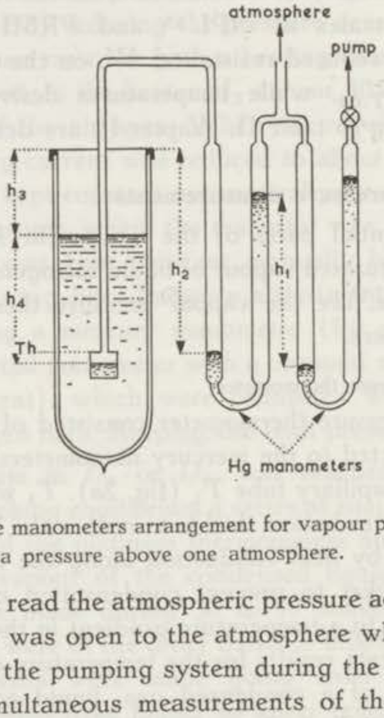

Fig. 4. Sketch of the manometers arrangement for vapour pressure measurements, specially at a pressure above one atmosphere.

During the simultaneous measurements of the pressure of the saturated vapour of liquid nitrogen in *Th* and the resistance of the platinum thermometers, the atmospheric pressure was measured about every 10 minutes. By plotting the measured pressure values as a function of time, it was possible to deduce the vapour pressure of the condensed nitrogen in *Th* at any time during the measurements. A disadvantage of the use of two manometers is that the inaccuracies of two sets of readings enter in the results. This is not very important in our case since the sensitivity is high for the nitrogen at a pressure equal or larger than one atmosphere (dp/dT at the boiling point is about 90 mm Hg per degree Kelvin).

For the measurements with apparatus A a cathetometer and an invar scale were used. For the measurements with apparatus B a cathetometer and a brass scale were used. The accuracy of the invar scale was better than 0.005 mm. The accuracy of the brass scale was better than 0.01 mm. All measured pressures have been corrected to mm Hg at 0°C and standard gravity (980.665 cm/s^2).

Using a mercury manometer and a cathetometer it is possible to measure the vapour pressure with an accuracy of 0.02 mm Hg. Therefore, temperatures between 63.142 and 85°K can be derived from measurements of the vapour pressure of nitrogen with an accuracy of nearly 1 m°K or better as dp/dT at 63.142 and 85°K are nearly 17 and 165 mm Hg per degree Kelvin respectively. Temperatures derived from the measured vapour pressures are denoted by T_p.

c. Thermomolecular pressure difference

A correction for the thermomolecular pressure difference has to be applied when the mean free path of the gas molecules is of the order of the diameter of the capillary tube which connects the vapour pressure thermometer reservoir Th to the manometer. This means that, at sufficiently low pressures there is a difference in pressure between the ends of the capillary tube when a temperature difference exists between Th and the manometer. In our case this correction is negligible.

d. Aerostatic correction

A correction due to the "aerostatic pressure head" of the gas column in the tube leading to the vapour pressure thermometer reservoir Th has been applied to the measured pressure. The exact calculation of this correction requires a knowledge of the temperature gradient along the tube. A sufficiently accurate correction can be calculated assuming that the gas in the part of the tube that was below the liquid surface of the bath has the density of the saturated vapour and that the temperature of the capillary between the surface of the liquid in the bath and the top of the cryostat varies quadratically[57] with the distance from the top of the cryostat. The mean temperature T_m is given by

$$T_m = \tfrac{2}{3} T_r + \tfrac{1}{3} T_l \qquad (2)$$

when $\dfrac{T - T_r}{T_l - T_r} = \dfrac{(h - h_r)^2}{h_r^2}$

T_1 is the temperature at the liquid surface of the bath

T_r is the temperature at a distance h above the liquid level.

T is the temperature at a distance h above the liquid level.

T_m has been used to obtain an approximation of the average density between the liquid level ($h = 0$) and the top of the cryostat ($h = h_r$).

The pressure correction Δp has been calculated as follows (see fig. 4):

$$\Delta p = \left[-h_1 \rho_{air}(T_r) - h_2 \rho_{N_2}(T_r) + h_3 \rho_{N_2}(T_m) + h_4 \rho_{N_2}(T_{Th}) \right] \frac{g}{\rho_0 g_0}$$

where Δp is expressed in mm Hg at 0°C and standard gravity when h is expressed in mm.

$\rho_{air}(T_r)$ is the density of the air column (h_1) at room temperature and atmospheric pressure

$\rho_{N_2}(T_r)$ is the density of the nitrogen column (h_2) at room temperature and at the measured pressure

$\rho_{N_2}(T_m)$ is the density of the nitrogen column (h_3) at the mean temperature T_m as calculated from eq. (2) and the measured pressure

$\rho_{N_2}(T_{Th})$ is the density of the nitrogen column (h_4) at saturation and at the temperature of the vapour pressure thermometer

ρ_0 is the density of the mercury at 0°C (13.5951 g/cm^3)

g_0 is the acceleration due to standard gravity (980.665 cm/s^2), and

g is the local acceleration of gravity.

The effect of the pressure correction on the measured temperature is given by

$$\Delta T = \Delta p \frac{dT}{dp}$$

where dp/dT can be taken from table III, chapter II. Fig. 5 shows the length of the nitrogen gas column h_4 causing an error of 1 m°K

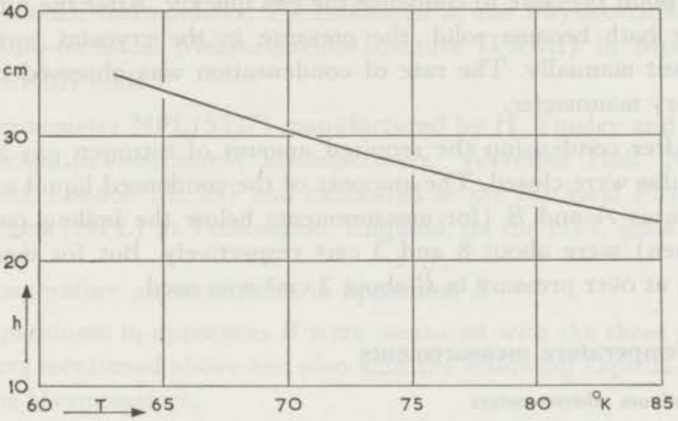

Fig. 5. The "aerostatic head" correction in a nitrogen vapour pressure thermometer. h is the height of the column of nitrogen vapour at saturated density that influences the measured temperature by 1 m°K.

in the measured temperature in the temperature region from 63 to 85°K. It is clear that the correction is small in this region.

e. The condensed nitrogen

The nitrogen condensed into the vapour pressure thermometer reservoir *Th* was supplied by the British Oxygen Company (Export Department, Cricklewood, London NW 2). According to the supplier the purity of this nitrogen is 99.998%. The nitrogen was received in glass bulbs of 2.5 l filled to one atmosphere. During measurements in apparatus *A*, four bulbs were connected together, while for apparatus *B* one bulb only was used. The nitrogen gas was condensed in *Th* as follows:

1. After filling the inner and outer dewars with liquid nitrogen from the laboratory stock, the evacuated lines which connected the nitrogen gas bulbs to *Th* and a mercury manometer were cleaned by admitting a small amount of gas in it and pumping again. This step was repeated two times to be sure that no impurities were left.

2. The nitrogen bulbs were connected to a mercury manometer to determine its pressure before condensation.

3. Then, the bulbs were connected to the reservoir *Th* and we started to reduce the pressure over the bath to a pressure below the triple point pressure to condense the gas quickly. After the nitrogen in the bath became solid, the pressure in the cryostat was kept constant manually. The rate of condensation was observed on the mercury manometer.

4. After condensing the required amount of nitrogen gas in *Th*, the bulbs were closed. The amounts of the condensed liquid used in apparatus *A* and *B* (for measurements below the boiling point of nitrogen) were about 8 and 3 cm^3 respectively. But for measurements at over pressure in *B* about 2 cm^3 was used.

6. Temperature measurements

a. Platinum thermometers

A strain-free-wound well annealed wire of pure platinum, enclosed in a capsule containing some helium gas, is a sensitive and very reliable instrument for obtaining accurate and reproducible temperature indications between 90 and 10°K. Much accurate information concerning the temperature dependence of the reduced resistance of platinum is available. At several laboratories platinum thermometers have been compared with a gas thermometer. Many other platinum thermometers have been compared with those calibrated with gas thermometers and in this way their calibrations between 90 and 10°K have been established.

The calibrations of the secondary platinum resistance thermometers rely either on comparison of new platinum thermometers with platinum thermometers calibrated with a gas thermometer (primary standard) or on calibrations at temperatures deduced from readings of a vapour pressure thermometer. In this way the temperature dependence of the resistance of many platinum thermometers for use below 90°K has been established.

1. Temperature measurements in apparatus *A*

Temperatures were measured in apparatus *A* with the following capsule-type platinum thermometers:

1) Thermometer LN1137601 manufactured by Leeds and Northrup Company (Philadelphia 44, Pa. U.S.A.) and calibrated at the

National Bureau of Standards (NBS) in Washington on the NBS-1955 scale.

2) A Russian thermometer, T_4, calibrated at the Physico-technical and Radio-technical Measurements Institute (PRMI) in Moscow on the PRMI scale.

3) Thermometer NPL153371 manufactured by H. Tinsley and Co., Ltd. (Scientific instrument manufacturers, Werndee Hall, South Norwood, London SE 25) and calibrated at the National Physical Laboratory (NPL) at Teddington, England, on the NPL scale.

2. Temperature measurements in apparatus *B*

Temperatures in apparatus *B* were measured with the three thermometers mentioned above and also with the following capsule-type platinum thermometers:

1) Thermometer NBS1575702, calibrated at NBS on the NBS-1955 scale.

2) Thermometer NPL153373 manufactured by Tinsley and calibrated at NPL on the NPL scale.

The last two thermometers NBS1575702 and NPL153373 are among eight platinum thermometers which were used in 1962 and 1963 for the comparison, at NPL and PRMI, of the NBS, NPL, PRMI and Pennsylvania State University (PSU)[58] scales.

From the reduced resistances, $W = R(T)/R(0°\text{C})$, the platinum thermometer temperatures could be derived on the individual scales, on the average reduced scale [55, 56], and on the CCT-64 scale (see section 7). These temperatures are denoted by T_n, $\bar{T}_{nr}$ and $T_{\text{CCT-64}}$ respectively. Most of our measurements were made with the thermometers LN1137601 and T_4, both being used in apparatus *A* and *B*. In apparatus *A*, the triple point measurements were made only with the last two thermometers because unfortunately one of the leads of the NPL153371 thermometer was broken inside the cryostat. Usually we measured the resistance $R(0°\text{C})$ of the platinum thermometers at the ice point before and after the measurements at liquid nitrogen temperatures.

Some basic data of all thermometers, which were used in our measurements, are given in table I.

TABLE I

Some basic data of all thermometers according to our measurements.

Pt thermometer	$R(0°C)$ Ω	$R(100°C)$ Ω	$10^3 \alpha$ $°C^{-1}$
LN1137601	25.53577	35.55971	3.92545
T_4	25.03484	34.86580	3.92691
NPL153371	25.37800	35.34240	3.92639
NPL153373	24.98309	34.79357	3.92684
NBS1575702	25.55999	35.64860	3.92578

b. Resistance measurements

To determine the resistances of platinum resistance thermometers, we used a Tinsley type 4363D Vernier potentiometer. With this potentiometer it is possible to obtain six or seven figures for the measured resistance. As a zero-detector we used a Zernike (Zc) galvanometer (Kipp, Delft, Netherlands) which gives a deflection of ½ mm per 10^{-8} V on a scale four meter distant from the galvanometer. This is within the limit of accuracy for our measurements.

For the present work, usually a measuring current of 2 mA has been used. For the resistance measurements an accuracy better than 1 m°K, which corresponds to $\approx 4 \times 10^{-6}$ of the resistance at 0°C, can be reached easily. Thermal EMF's are eliminated by reversing the currents through the thermometer and the potentiometer.

7. Temperature scale from 91 to 10°K

a. General introduction

The secondary instruments that have been most practical for reproducible measurements of low temperatures are the platinum thermometer, the thermocouple, the magnetic thermometer and the vapour-pressure thermometer. The vapour-pressure thermometer can be used only in limited temperature ranges, but it is very valuable for calibrations since it may yield temperatures throughout its range which are, in effect, a continuous series of secondary fixed points related to each other by a thermodynamic p-T relation. The magnetic thermometer is most useful at very low temperatures. The thermocouple has been extensively used and possesses several desirable characteristics. The resistance thermometer, although unable to compete with the thermocouple in simplicity, low cost, or absence of heat dissipation, does possess a very considerable advantage in its sensitivity and high reproducibility.

b. Temperature scales up to 1964

Measurements with a gas thermometer between 10 and 90°K were made at several institutes; e.g., National Bureau of Standards in Washington, National Physical Laboratory in Teddington, Pennsylvania State University, Physico-technical and Radio-technical Measurements Institute in Moscow. At each institute the results were considered as the establishment of a private or individual scale maintained by a few primary standard platinum thermometers or recorded in the results of vapour pressure measurements.

Individual scales can be compared conveniently by comparison of platinum thermometers, calibrated on the scales of the different institutes, at a large number of temperatures. These individual scales differ because:

a. For the derivation of the gas thermometer temperatures, different values have been used for the ice point or the oxygen boiling point which were used as reference points for the gas thermometer.

b. The corrections used for the non-ideality of the gas and for the thermal-expansion of the gas thermometer reservoir were not always the same.

c. Individual errors can occur in the gas thermometer measurements.

Today, the main individual scales, for use below 91°K, are those of NPL, NBS, PRMI, and PSU. These four scales differ appreciably in temperature indication.

1. The average reduced scale $\bar{T}_{nr}$ [55, 56]

In June 1958 the Advisory Committee for Thermometry of the International Committee of Weights and Measures (Comité Consultatif de Thermométrie (CCT) auprès du Comité International des Poids et Mesures) decided to organize a comparison of platinum resistance thermometers calibrated at laboratories specialized for measurements in the temperature range between 20 and 90°K and to prepare detailed proposals for the extension of the International Practical Temperature scale (IPTS).

In September 1962 the CCT established two working groups for improvements and extension of the International Practical Temperature Scale. One of these groups was charged to prepare a report on propositions that could lead to a decision to extend the IPTS tc temperatures between 20 and 90°K.

As a consequence of this assignment, Working group II considered it as its task to recommend a relation (table) between the reduced resistances $R(T)/R(0°\mathrm{C})$ of platinum resistance thermometers and thermodynamic temperatures between the boiling point of oxygen and a hydrogen point (boiling point or triple point) and to recommend a procedure for the calibration of platinum resistance thermometers over this range of temperature.

To realize the decision taken by the CCT in 1958 and obtain a generally acceptable relation for $R(T)/R(273.15°\mathrm{K})$, each of the four institutes mentioned provided two calibrated thermometers and a comparison of the eight resistance thermometers was carried out at NPL and PRMI in 1962 and 1963. At NPL the eight thermometers were compared at 32, and at PRMI at 34 temperatures between 10 and 91°K. Temperatures on the individual scales are defined with tables. In these tables the reduced resistance, $W(T) = R(T)/R(0°\mathrm{C})$, is given as a function of temperature, or the temperature is given as a function of the reduced resistance. As a result of the comparisons, the weighted average $\overline{W}$ of the reduced resistances has been obtained as a function of the average reduced temperature $\overline{T}_{\mathrm{nr}}$ for all the 66 comparison points between 10 and 91°K.

During the comparison it appeared that two of the chosen eight thermometers did not reproduce so well as the other six. Therefore the results obtained with these two thermometers were not used to obtain $\overline{W}$. In taking the average for the remaining six thermometers the results obtained for the thermometers provided by NBS and PSU were given half weight since these thermometers were provided by the same manufacturer. The scales of the four institutes were given equal weight. Hence, we have

$$\overline{W} = \tfrac{1}{3}\Big[\tfrac{1}{2}\Big\{W_{\mathrm{NBS}1575702} + \tfrac{1}{2}\left(W_{\mathrm{PSU}1577533} + W_{\mathrm{PSU}1577534}\right)\Big\} + W_{\mathrm{PRMI},\,\mathrm{T}_2} + \tfrac{1}{2}\left(W_{\mathrm{NPL}153372} + W_{\mathrm{NPL}153373}\right)\Big] \qquad (3)$$

$$\overline{T}_{\mathrm{n}} = \tfrac{1}{4}\Big[T_{\mathrm{NBS\text{-}1939},\,1575702} + T_{\mathrm{PRMI},\,\mathrm{T}_2} + \tfrac{1}{2}\left(T_{\mathrm{PSU}1577533} + T_{\mathrm{PSU}1577534}\right) + \tfrac{1}{2}\left(T_{\mathrm{NPL}153372} + T_{\mathrm{NPL}153373}\right)\Big] \qquad (4)$$

where 1575702, 1577533, 1577534, T_2, 153372 and 153373 are the identifying numbers of the platinum thermometers.

To bring the four scales closer to each other, the scales were reduced in such a way that the normal boiling points of oxygen and of normal hydrogen recommended by each institute for use with its own scale coincide with the values recommended by the Comité Consultatif de Thermométrie (CCT) at the Bureau International des Poids et Mesures in 1962. The recommended boiling points of oxygen and normal hydrogen are given in table II.

TABLE II

The boiling points of oxygen and normal hydrogen recommended by the Comité Consultatif de Thermométrie in 1962 and the data given by different institutes on their own scales.

	CCT 1964 °K	NBS (1939) °K	NPL °K	PRMI °K	PSU °K
n-H_2	20.384	20.392^5	20.387^5	20.394	20.365
O_2	90.17	90.190	90.180	90.100	90.151

The corresponding reduction formulae for the individual scales are:

$$T_{\mathrm{NBS\text{-}1939,\,red}} = T_{\mathrm{NBS\text{-}1939}} - 0.00514\,^\circ\mathrm{K} - 0.0001648\,T \qquad (5)$$

$$T_{\mathrm{NPL,\,red}} = T_{\mathrm{NPL}} - 0.00160\,^\circ\mathrm{K} - 0.0000931\,T \qquad (6)$$

$$T_{\mathrm{PMRI,\,red}} = T_{\mathrm{PRMI}} - 0.00445\,^\circ\mathrm{K} - 0.0002723\,T \qquad (7)$$

$$T_{\mathrm{PSU,\,red}} = T_{\mathrm{PSU}} + 0.01900\,^\circ\mathrm{K}. \qquad (8)$$

Therefore,

$$\overline{T}_{\mathrm{nr}} = \overline{T}_{\mathrm{n}} + 0.001952\,^{\circ}\mathrm{K} - 0.0001325\,T. \qquad (9)$$

Eqs. (5), (6), (7) and (8) bring the individual scales close to each other. The remaining deviations of the reduced scales from their average are everywhere between 17 and 90.2°K smaller than 10 m°K. The deviations of the individual W and T values from the average $\overline{W}$ and $\overline{T}_{\mathrm{nr}}$ values at the 66 comparison points were obtained from the intercomparisons at NPL and PRMI. For temperatures between the 66 points graphical interpolation can be used to obtain the deviations at any desired temperature.

2. The CCT-64 table [43]

At PRMI Mrs. Orlova et al. prepared several tables to represent $\overline{T}_{\mathrm{nr}}\,(\overline{W})$ and $\overline{W}\,(\overline{T}_{\mathrm{nr}})$ in a smoothed way. These tables are in close agreement with the results of the comparisons of platinum thermometers at NPL and at PRMI. One of these tables called BI table has been recommended by the CCT in 1964 for provisional use. It gives T_{BI} as a function of $\overline{W}$. At the 66 temperatures at which the scale comparisons were made, T_{BI} is nearly but not exactly equal to $\overline{T}_{\mathrm{nr}}$. T_{BI} is the temperature corresponding to $\overline{W}$ according to the BI table.

At a meeting, in September 1964, at the Bureau International des Poids et Mesures at Sèvres, the Comité Consultatif de Thermométrie (CCT) recommended the BI table as a provisional table, to be used for interpolation of $W(=R(T)/R(0^{\circ}\mathrm{C}))$ values of platinum resistance thermometers between fixed points, and called it CCT-64 table. Although it was meant by its authors as a table to be used for interpolation, it was realized by the Comité Consultatif de Thermométrie that the CCT-64 table can also be used to define a temperature scale in terms of the reduced resistance of a number of platinum thermometers. It gives $T_{\mathrm{CCT\text{-}64}}$ in °K as a function of $\overline{W}$. Differences between $T_{\mathrm{CCT\text{-}64}}$ and $\overline{T}_{\mathrm{nr}}$ have been given by Orlova and others [43] in a table, and are shown for temperatures between 63° and 91°K in fig. 6.

When for a given thermometer $\overline{W} - W_{\mathrm{x}}$ as a function of temperature or of the reduced resistance has been obtained from comparisons with a standard platinum thermometer at a sufficient number of temperatures, it is easy to obtain $(\overline{W}-W_x)$ for an arbitrary measured value of W_x in the calibration region by gra-

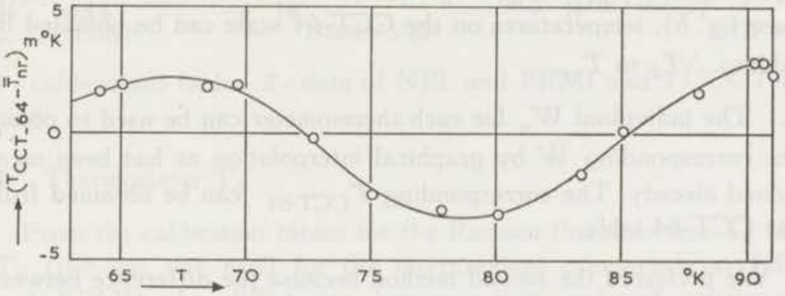

Fig. 6. Differences between $T_{CCT\text{-}64}$ and the average reduced scale $\overline{T}_{nr}$ in the temperature region from 63 up to 91°K.

phical interpolation and then to obtain $T_{CCT\text{-}64}$ with the aid of the CCT-64 table.

c. Reduction of our measured temperature on the individual scales to the CCT-64 scale

Since we used for our temperature measurements platinum thermometers calibrated on their own individual scale (NBS, NPL or PRMI see 6*a*), it is preferable to reduce the different temperatures T_n on the individual scales immediately to temperatures on the CCT-64 scale. Firstly, to see directly the differences between the temperature indications with the different thermometers and secondly to compare temperatures obtained from our thermodynamic *p-T* relation for nitrogen with temperatures on the CCT-64 scale. In fact, it is possible to reduce T_n to $T_{CCT\text{-}64}$ in the following two different way:

1. *a.* By deriving the temperatures T_n from the measured reduced resistance W_n, for each thermometer on its own scale.

b. By applying eq. (1), (2), or (3) to obtain the individual reduced temperatures T_{nr}.

c. By using a smoothed graphical interpolation of the differences $\Delta T_1 = \overline{T}_{nr} - T_{nr}$, from the data obtained at NPL and PRMI, temperatures on the average reduced temperature scale can be obtained by adding $\triangle T_1$ to T_{nr}.

d. By using a smoothed graphical interpolation of the differences $\triangle T_2 = T_{\mathrm{CCT\text{-}64}} - \overline{T}_{\mathrm{nr}}$, given by Orlova at 66 temperatures (see fig. 6), temperatures on the CCT-64 scale can be obtained by adding $\triangle T_2$ to $\overline{T}_{\mathrm{nr}}$.

2. The individual W_{n} for each thermometer can be used to obtain the corresponding $\overline{W}$ by graphical interpolation as has been mentioned already. The corresponding $T_{\mathrm{CCT\text{-}64}}$ can be obtained from the CCT-64 table.

We preferred the second method because the difference between reduced resistances of platinum thermometers is a smooth function of temperature, which is not always the case for the differences ($T_{\mathrm{CCT\text{-}64}} - T_{\mathrm{nr}}$). Details of the calculation for each thermometer will be given below.

1. Thermometer NBS1575702

The thermometer was used for the international comparison at NPL and PRMI. Its reduced resistance values and the corresponding $\overline{W}$ values at the 66 comparison points are available. Therefore, using a smoothed graphical interpolation of the differences $\overline{W} - W_{1575702}$ as obtained from the data of NPL and PRMI, values for the average reduced resistance were deduced for all our measured reduced resistances obtained with this thermometer. From these values for the average reduced resistance, temperatures $T_{\mathrm{CCT\text{-}64}}$ were derived from the CCT-64 scale.

2. Thermometer LN1137601

From the calibration tables for thermometers LN1137601 and NBS1575702 the differences between their reduced resistances, $\triangle W = W_{\mathrm{NBS1575702}} - W_{\mathrm{LN1137601}}$, as a function of temperature were deduced in the considered region. Adding of the measured $W_{\mathrm{LN1137601}}$ and $\triangle W$ gives $W_{\mathrm{NBS1575702}}$ at the measured temperatures.

From these $W_{\mathrm{NBS1575702}}$ values, temperatures in the CCT-64 scale were derived in the same way as mentioned before. The method of calculation for $T_{\mathrm{CCT\text{-}64}}$ using thermometer LN can be given in a scheme as follows:

$$W_{\mathrm{LN1137601}}^{\mathrm{(exp.)}} \xrightarrow{1} W_{\mathrm{NBS1575702}} \xrightarrow{2} W \xrightarrow{3} T_{\mathrm{CCT\text{-}64}}$$

1 - calibrations tables, 2 - data of NPL and PRMI and 3 - CCT-64 table.

3. Thermometer T_4

From the calibration tables for the Russian thermometers T_4 and T_2 (the last one used for the international comparison at NPL and PRMI) the differences between their reduced resistances $\triangle W = W_{T_2} - W_{T_4}$ as a function of temperature were deduced in the considered region. Using a smoothed graphical interpolation of these $\triangle W$ values we obtained the $\triangle W$ values at the measured temperatures. Adding of the measured W_{T_4} and $\triangle W$ gives W_{T_2} at the measured temperatures.

From these W_{T_2} values, temperatures on the CCT-64 scale were derived in the same way as mentioned for the NBS1575702 thermometer.

4. Thermometer NPL153373

This thermometer was used also for the international comparison at NPL and PRMI. Therefore, our temperatures measured with it were derived in the CCT-64 scale in the same way as mentioned for the thermometer NBS1575702.

5. Thermometer NPL153371

For thermometers NPL153372 and NPL153373 the difference between the reduced resistances, $\triangle W = W_{153373} - W_{153371}$, as a function of temperature was deduced from the calibration data given by NPL. Adding of the measured values of W_{153371} and $\triangle W$ gives W_{153373}. From these W_{153373} values, temperatures in the CCT-64 scale were derived as mentioned above for the thermometer NBS1575702.

8. Experimental results

a. General results

The measurements can be divided into three series. The thermometers T_4 and LN1137601 were used at all the measured temperatures. We measured 42 temperatures with both of the thermometers T_4 and LN1137601 while only 16 temperatures were measured with thermometer NPL153371. Each of the thermometers NPL153373 and NBS1575702 was measured at 10 temperatures in the second series. The total number of temperatures measured between about 63 and 85°K is 120.

The experiment consisted of simultaneous measurements of the vapour pressure of nitrogen and of the resistances of platinum thermometers. Temperatures, T_p, were derived from the measured vapour pressure using table II, chapter II, and from the measured reduced resistance, $W = R(T)/R(0°\mathrm{C})$, temperatures $T_{\mathrm{CCT\text{-}64}}$ were derived in the way described in section 7*c*. The measured pressures and temperatures and the differences between T_p values and the corresponding $T_{\mathrm{CCT\text{-}64}}$ values are given in tables III, IV, V, VI and VII and shown in figs. 7, 8, 9, 10 and 11 respectively for the five thermometers which were used for the experiment.

The pressures given in tables III, IV, V, VI and VII are the pressures in the vapour pressure thermometer reservoir *Th*, corrected for the aerostatic pressure head. The aerostatic head corrections were calculated as mentioned in section 5*d*. These pressures are reduced to mm Hg at 0°C and standard gravity (980.665 cm/s^2).

A smooth curve was drawn in figs. 7, 8, 9, 10 and 11. The curve represents a smooth average of $T_{\mathrm{CCT\text{-}64}} - T_p$ according to tables XI and II, chapter II, respectively. Details about table XI are given in section 9. The maximum difference between $T_{\mathrm{CCT\text{-}64}}$ and T_p is, according to this smooth curve, nowhere more than 1.3 m°K between the boiling point and the triple point, while above the boiling point the deviation increases gradually up to 7 m°K at 85°K.

b. The boiling point

For the measured vapour pressure values, corresponding tempe-

TABLE III

The measured vapour pressure of liquid nitrogen, the corresponding temperature $T_{CCT\text{-}64}$, according to thermometer T_4, the thermodynamic temperature T_p, according to table II, chapter II, and the temperature difference $\triangle T_1 = T_{CCT\text{-}64} - T_p$. $\triangle T_2 = T_p$ (table XI)—$T_{CCT\text{-}64}$.

Series	Date	p mm Hg, 0°C	T_p °K	$T_{CCT\text{-}64}$ °K	$\triangle T_1$ m°K	$\triangle T_2$ m°K
	7-11-63	772.068	77.4723	77.4727	+ 0.4	— 0.6
	8-11	343.818	71.1897	71.1900	+ 0.3	+ 0.8
		457.042	73.2700	73.2710	+ 1.0	0.0
	11-11	132.272	65.0648	65.0662	+ 1.4	— 0.5
		182.631	66.9997	67.0014	+ 1.7	— 0.6
	12-11	793.690	77.7084	77.7079	— 0.5	+ 0.1
		483.768	73.7015	73.7024	+ 0.9	— 0.1
	13-11	154.548	65.9826	65.9837	+ 1.1	0.0
		215.549	68.0438	68.0452	+ 1.4	0.0
		290.198	70.0109	70.0122	+ 1.3	0.0
	14-11	808.710	77.8694	77.8701	+ 0.6	— 1.1
	15-11	93.922	63.1420	63.1425	+ 0.5	— 0.5
I	30-11	797.160	77.7457	77.7452	— 0.5	+ 0.2
	2-12	93.920	63.1419	63.1423	+ 0.4	— 0.4
	21- 1-64	806.615	77.8470	77.8471	+ 0.1	— 0.4
		298.808	70.2111	70.2126	+ 1.5	— 0.2
		392.262	72.1366	72.1381	+ 1.5	— 0.3
		449.092	73.1379	73.1390	+ 1.1	— 0.1
	22- 1	107.365	63.8781	63.8782	+ 0.1	+ 0.3
		339.903	71.1087	71.1099	+ 1.2	0.0
		509.315	74.0970	74.0977	+ 0.7	0.0
	23- 1	574.692	75.0434	75.0442	+ 0.8	— 0.2
		648.831	76.0214	76.0216	+ 0.2	+ 0.1
		763.009	77.3720	77.3719	— 0.1	0.0
	9- 9-64	159.800	66.1835	66.1842	+ 0.7	+ 0.4
		385.240	72.0053	72.0064	+ 1.1	0.0
		571.243	74.9957	74.9962	+ 0.5	0.0
	10- 6	792.331	77.6937	77.6942	+ 0.5	— 0.8
		110.077	64.0175	64.0182	+ 0.7	— 0.3
II	11- 6	949.257	79.2761	79.2755	— 0.6	— 0.4
		1148.009	81.0177	81.0156	— 2.1	— 0.2
		1404.243	82.9552	82.9513	— 3.9	— 0.3
		1630.181	84.4546	84.4485	— 6.1	0.0
	12- 6	792.041	77.6905	77.6907	+ 0.2	— 0.5
	22- 9	851.635	78.3175	78.3173	— 0.2	— 0.4
	23- 9	769.146	77.4400	77.4404	+ 0.4	— 0.5
		1367.307	82.6933	82.6898	— 3.5	— 0.5
		1610.204	84.3286	84.3233	— 5.3	— 0.7
III		1461.036	83.3481	83.3437	— 4.4	— 0.2
	24- 9	1143.910	80.9842	80.9819	— 2.3	0.0
		1013.364	79.8657	79.8637	— 2.0	+ 0.5
		754.870	77.2810	77.2811	+ 0.1	— 0.2

TABLE IV

The measured vapour pressure of liquid nitrogen, the corresponding temperature $T_{\mathrm{CCT\text{-}64}}$, according to thermometer LN1137601, the thermodynamic temperature T_{p}, according to table II, chapter II, and the temperature difference $\triangle T_1 = T_{\mathrm{CCT\text{-}64}} - T_{\mathrm{p}}$. $\triangle T_2 = T_{\mathrm{p}}$ (table XI)—$T_{\mathrm{CCT\text{-}64}}$.

Series	Date	p mm Hg, 0°C	T_{p} °K	$T_{\mathrm{CCT\text{-}64}}$ °K	$\triangle T_1$ m°K	$\triangle T_2$ m°K
	7-11-63	772.050	77.4721	77.4740	+ 1.9	— 2.0
	8-11	343.822	71.1897	71.1905	+ 0.8	+ 0.4
		456.955	73.2686	73.2695	+ 0.9	0.0
	11-11	132.303	65.0662	65.0653	— 0.9	+ 1.8
		182.613	66.9991	67.0000	+ 0.9	— 0.1
	12-11	793.673	77.7082	77.7082	0.0	— 0.3
		483.823	73.7024	73.7032	+ 0.8	0.0
	13-11	154.556	65.9830	65.9838	+ 0.8	+ 0.2
		215.519	68.0429	68.0443	+ 1.4	0.0
		290.273	70.0127	70.0138	+ 1.1	+ 0.1
	14-11	809.753	77.8805	77.8822	+ 1.7	— 2.1
	15-11	93.922	63.1420	63.1421	+ 0.1	— 0.1
I	30-11	797.843	77.7531	77.7522	— 0.9	+ 0.6
	2-12	93.920	63.1419	63.1409	— 1.0	+ 1.0
	21- 1-64	807.001	77.8512	77.8532	+ 1.7	— 2.4
		298.788	70.2107	70.2125	+ 1.8	— 0.6
		392.448	72.1401	72.1419	+ 1.8	— 0.6
		449.224	73.1401	73.1425	+ 2.4	— 1.3
	22- 1	107.415	63.8807	63.8817	+ 1.0	— 0.7
		339.918	71.1090	71.1114	+ 2.4	— 1.2
		509.459	74.0992	74.1021	+ 2.9	— 2.2
	23- 1	574.868	75.0459	75.0489	+ 3.0	— 2.4
		648.873	76.0219	76.0242	+ 2.3	— 2.0
		763.006	77.3719	77.3742	+ 2.3	— 2.4
	9- 6-64	159.791	66.1831	66.1843	+ 1.2	— 2.5
		385.396	72.0083	72.0075	— 0.8	+ 1.8
		571.357	74.9973	74.9965	— 0.8	+ 1.3
	10- 6	792.296	77.6933	77.6937	+ 0.4	— 0.7
		110.086	64.0179	64.0173	— 0.6	+ 1.0
II	11- 6	948.929	79.2730	79.2726	— 0.4	— 0.6
		1147.727	81.0154	81.0136	— 1.8	— 0.5
		1403.888	82.9527	82.9486	— 4.1	— 0.1
		1629.942	84.4531	84.4471	— 6.0	0.0
	12- 6	792.174	77.6920	77.6925	+ 0.5	— 0.8
	22- 9	851.574	78.3169	78.3162	— 0.7	+ 0.1
	23- 9	768.865	77.4369	77.4360	— 0.9	+ 0.8
		1367.280	82.6931	82.6882	— 4.9	+ 0.9
		1610.173	84.3284	84.3216	— 6.8	— 0.8
III		1461.354	83.3503	83.3471	— 3.2	— 1.4
	24- 9	1143.463	80.9806	80.9787	— 1.9	— 0.4
		1013.453	79.8665	79.8627	— 3.8	+ 2.3
		754.654	77.2786	77.2771	— 1.5	+ 1.4

TABLE V

The measured vapour pressure of liquid nitrogen, the corresponding temperature $T_{\text{CCT-64}}$, according to thermometer NPL153371, the thermodynamic temperature T_p, according to table II, chapter II, and the temperature difference $\triangle T_1 = T_{\text{CCT-64}} - T_p$. $\triangle T_2 = T_p$ (table XI)$-T_{\text{CCT-64}}$.

Series	Date	p mm Hg, 0°C	T_p °K	$T_{\text{CCT-64}}$ °K	$\triangle T_1$ m°K	$\triangle T_2$ m°K
	7-11-63	771.095	77.4616	77.4607	— 0.9	+ 0.8
		772.310	77.4750	77.4744	— 0.6	+ 0.4
	8-11	343.708	71.1874	71.1879	+ 0.5	+ 0.7
		456.414	73.2596	73.2599	+ 0.3	+ 0.7
I	11-11	132.267	65.0646	65.0667	+ 2.1	— 1.2
		182.708	67.0023	67.0040	+ 1.7	— 0.6
	12-11	793.946	77.7111	77.7099	— 1.2	+ 0.9
		793.634	77.7078	77.7068	— 1.0	+ 0.6
	22- 9-64	851.622	78.3174	78.3167	— 0.7	+ 0.1
	23- 9	769.008	77.4385	77.4380	— 0.5	+ 0.4
		1367.098	82.6918	82.6887	— 3.1	— 0.9
		1610.126	84.3281	84.3211	— 7.0	+ 1.0
III		1461.602	83.3520	83.3473	— 4.7	0.0
	24- 9	1144.412	80.9883	80.9833	— 5.0	+ 2.7
		1013.132	79.8636	79.8604	— 3.2	+ 1.8
		754.845	77.2807	77.2803	— 0.4	+ 0.3

TABLE VI

The measured vapour pressure of liquid nitrogen, the corresponding temperature $T_{\text{CCT-64}}$, according to thermometer NBS1575702, the thermodynamic temperature T_p, according to table II, chapter II, and the temperature difference $\triangle T_1 = T_{\text{CCT-64}} - T_p$. $\triangle T_2 = T_p$ (table XI)$-T_{\text{CCT-64}}$.

Series	Date	p mm Hg, 0°C	T_p °K	$T_{\text{CCT-64}}$ °K	$\triangle T_1$ m°K	$\triangle T_2$ m°K
	9- 6-64	159.802	66.1835	66.1842	+ 0.7	+ 0.5
		385.174	72.0041	72.0053	+ 1.2	— 0.2
		571.096	74.9937	74.9943	+ 0.6	0.0
	10- 6	792.260	77.6929	77.6935	+ 0.6	— 0.9
		110.003	64.0137	64.0140	+ 0.3	+ 0.2
II	11- 6	949.363	79.2771	79.2759	— 1.2	+ 0.1
		1148.304	81.0201	81.0175	— 2.6	+ 0.3
		1405.377	82.9631	82.9576	— 5.5	+ 1.4
		1629.780	84.4521	84.4465	— 5.6	— 0.5
	12- 6	791.805	77.6880	77.6872	— 0.8	+ 0.5

TABLE VII

The measured vapour pressure of liquid nitrogen, the corresponding temperature $T_{\text{CCT-64}}$, according to thermometer NPL153373, the thermodynamic temperature T_p, according to table II, chapter II, and the temperature difference $\triangle T_1 = T_{\text{CCT-64}} - T_p$. $\triangle T_2 = T_p$ (table XI)$-T_{\text{CCT-64}}$.

Series	Date	p mm Hg, 0°C	T_p °K	$T_{\text{CCT-64}}$ °K	$\triangle T_1$ m°K	$\triangle T_2$ m°K
III	9- 6-64	159.806	66.1837	66.1844	+ 0.7	+ 0.4
		385.150	72.0036	72.0044	+ 0.8	+ 0.3
		571.277	74.9962	74.9970	+ 0.8	— 0.3
	10- 6	792.402	77.6945	77.6949	+ 0.4	— 0.8
		110.139	64.0206	64.0199	— 0.7	+ 1.2
	11- 6	949.151	79.2751	79.2747	— 0.4	— 0.7
		1147.518	81.0137	81.0119	— 1.8	— 0.5
		1403.463	82.9497	82.9459	— 3.8	— 0.4
		1630.350	84.4557	84.4501	— 5.6	— 0.5
	12- 6	792.294	77.6933	77.6943	+ 1.0	— 1.3

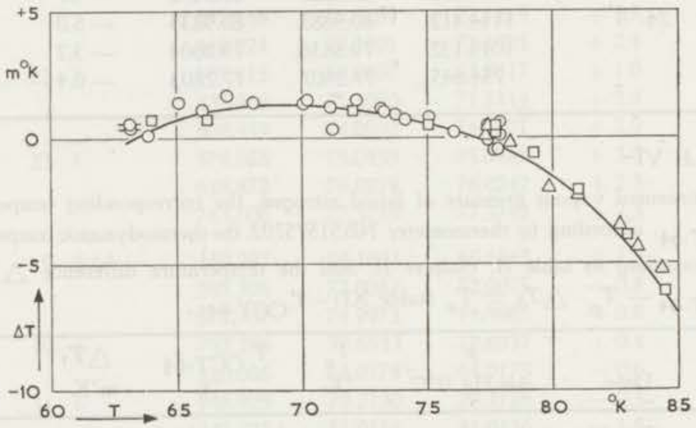

Fig. 7. Differences between temperatures in the CCT-64 scale, according to the thermometer T₄, and temperatures T_p deduced from vapour pressure measurements using table II, chapter II.

$\triangle T = T_{\text{CCT-64}} - T_p$

○ First series (Apparatus *A*)

□ Second series (Apparatus *B*)

△ Third series (Apparatus *B*)

—○— Triple point (apparatus *A*)

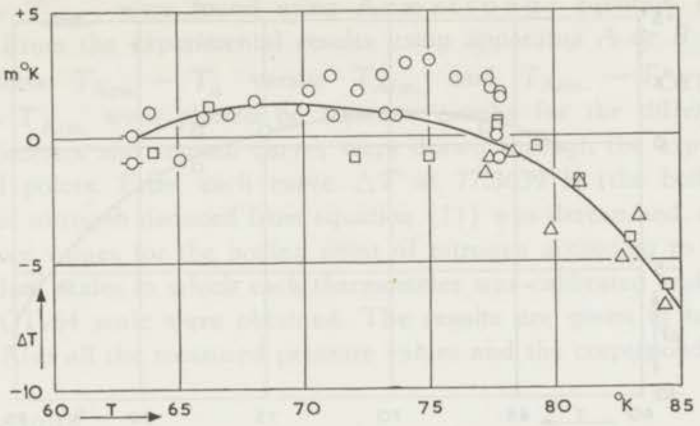

Fig. 8. Differences between temperatures in the CCT-64 scale, according to the thermometer LN1137601, and temperatures T_p deduced from vapour pressure measurements using table II, chapter II.

$\triangle T = T_{\mathrm{CCT\text{-}64}} - T_p$

○ First series (Apparatus *A*)
□ Second series (Apparatus *B*)
△ Third series (Apparatus *B*)
—○— Triple point (apparatus *A*)

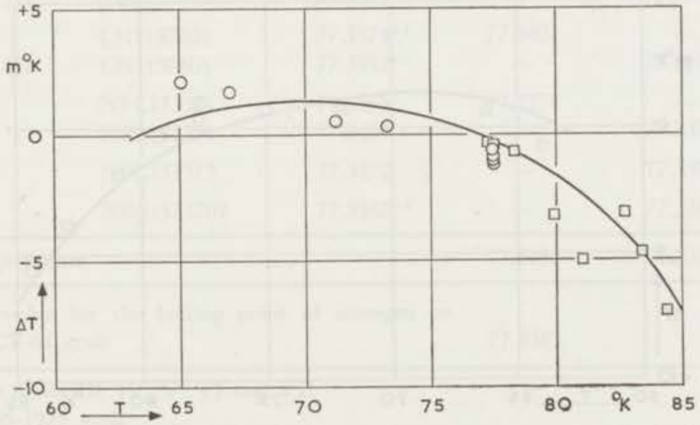

Fig. 9. Differences between temperatures in the CCT-64 scale, according to the thermometer NPL153371, and temperatures T_p deduced from vapour pressure measurements using table II, chapter II.

$\triangle T = T_{\mathrm{CCT\text{-}64}} - T_p$

○ First series (Apparatus *A*)
□ Third series (Apparatus *B*)

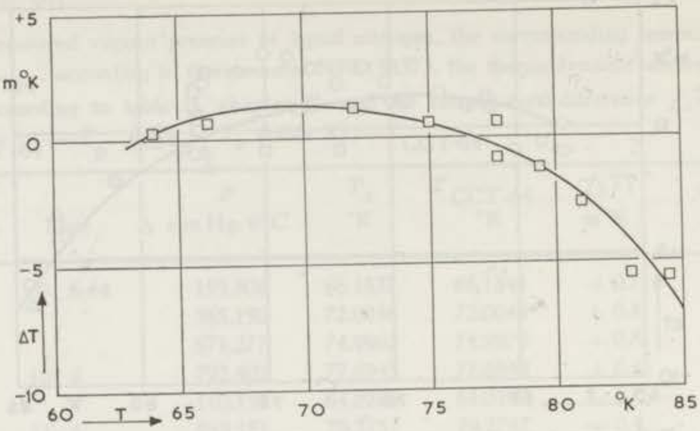

Fig. 10. Differences between temperatures in the CCT-64 scale, according to the thermometer NBS1575702, and temperatures T_p deduced from vapour pressure measurements using table II, chapter II.

$\triangle T = T_{\text{CCT-64}} - T_p$

☐ Second series (Apparatus *B*)

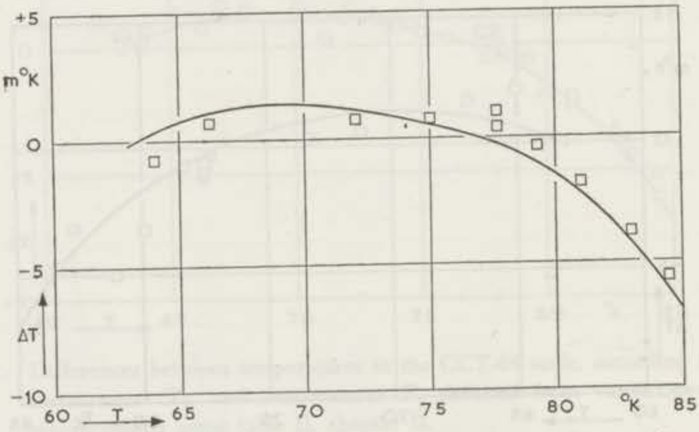

Fig. 11. Differences between temperatures in the CCT-64 scale, according to the thermometer NPL153373, and temperatures T_p deduced from vapour pressure measurements using table II, chapter II.

$\triangle T = T_{\text{CCT-64}} - T_p$

☐ Second series (Apparatus *B*)

ratures $T_{\text{Arm.}}$ were found using Armstrong's equation (eq. (1)). From the experimental results using apparatus A or B the deviations $T_{\text{Arm.}} - T_{\text{n}}$ versus $T_{\text{Arm.}}$ and $T_{\text{Arm.}} - T_{\text{CCT-64}}$ versus $T_{\text{Arm.}}$ were plotted on separate graphs for the different thermometers and smooth curves were drawn through the experimental points. From each curve $\triangle T$ at 77.3639°K (the boiling point of nitrogen deduced from equation (1)) was determined, and therefore values for the boiling point of nitrogen according to the individual scales in which each thermometer was calibrated and on the CCT-64 scale were obtained. The results are given in table VIII. Also all the measured pressure values and the corresponding

TABLE VIII

The values obtained for the boiling point of nitrogen according to the different thermometers.

Series*	Thermometer	T_{n}(°K)	$T_{\text{CCT-64}}$(°K)	
			Apparatus A	Apparatus B
I	T_4	77.3619	77.3384	—
II and III	T_4	77.3621	—	77.3386
I	LN1137601	77.3574**	77.3401	—
II and III	LN1137601	77.3552**	—	77.3379
I	NPL153371	77.3455	77.3374	—
III	NPL153371	77.3459	—	77.3378
II	NPL153373	77.3472	—	77.3391
II	NBS1575702	77.3562**	—	77.3385
Average values			77.3386	77.3384
Mean value for the boiling point of nitrogen on the CCT-64 scale			77.3385	

* See tables III, IV, V, VI and VII
** NBS-1955 scale

$T_{\text{CCT-64}}$ values according to the five thermometers were represented, using a least squares procedure, with an equation similar to eq. (10) given in section 9. According to this representation the normal boiling point of nitrogen is 77.3386°K on the CCT-64 scale. This value (77.3386°K) is in excellent agreement with the mean value (77.3385°K) on the CCT-64 scale, deduced with the other method (see table VIII). The estimated uncertainty in the boiling point of nitrogen in the CCT-64 scale is according to our results within ± 1 m°K. The difference between our values for the boiling point of nitrogen obtained with apparatuses *A* and *B* is 0.2 m°K only as can be seen from table VIII.

Armstrong found for the boiling point of nitrogen the value 77.3640°K on the NBS-1939 scale. This value corresponds to 77.3365°K on the CCT-64 scale which is lower than our mean value (77.3385°K) by 2.0 m°K. It is very satisfactory that the difference is so small. According to the data given by Lovejoy[60] the boiling point of nitrogen is 77.3547°K on the NBS-1955 scale, which corresponds to 77.3372°K on the CCT-64 scale. This value (77.3372°K) is in good agreement with our value (77.3385°K).

c. The triple point

The triple point pressure and temperature were measured with apparatus *A* by allowing the equilibrium vessel *Th* to warm up slowly through the triple point. Two experiments were made on different days, using different amounts of condensed nitrogen in *Th* (apparatus *A*). The pressure was measured with a mercury manometer. The values obtained for the triple point pressure are 93.922 and 93.920 mm Hg at 0°C and standard gravity, $g = 980.665$ cm/s^2. The triple point temperature was measured directly with the platinum resistance thermometers T_4 and LN1137601. The measured triple point temperatures and pressures are given in table IX. Thermometer T_4 reproduced very well, as can be seen from table IX. Thermometer LN1137601 did not reproduce so accurately. In the first experiment the triple point temperature (63.1421°K on the CCT-64 scale) measured with LN1137601 is in good agreement with that of thermometer T_4 (63.1425°K). But in the second experiment, it gives the value 63.1409°K (on the CCT-64 scale) which is not in agreement with the value obtained with thermometer T_4 (63.1423°K) nor with pressure values measured for the triple point. Anyhow, its reproducibility is within the accuracy limits of the other measurements with this thermometer. The

TABLE IX

The values obtained for the triple point temperature and pressure of nitrogen with the different thermometers.

Date	Thermometer	T_n (°K)	$T_{CCT\text{-}64}$ (°K)	p (mm Hg, 0°C)
15.11.1963	T_4	63.1601	63.1425	93.922
2.12.1963	T_4	63.1599	63.1423	93.920
Average $T_{tr.p}$ of N_2 according to the PRMI thermometer		63.1600	63.1424	
15.11.1963	LN1137601	63.1492	63.1421	93.922
2.12.1963	LN1137601	63.1480	63.1409	93.920
Average $T_{tr.p}$ of N_2 according to the LN thermometer		63.1486 (NBS-1955 scale)	63.1415	
Mean value for the triple point pressure and temperature of nitrogen			63.1420	93.921

algebraic mean value (63.1420°K on the CCT-64 scale) of the measured temperatures for the triple point, with the thermometers T_4 and LN1137601, is chosen for the final result. Fig. 12 shows the

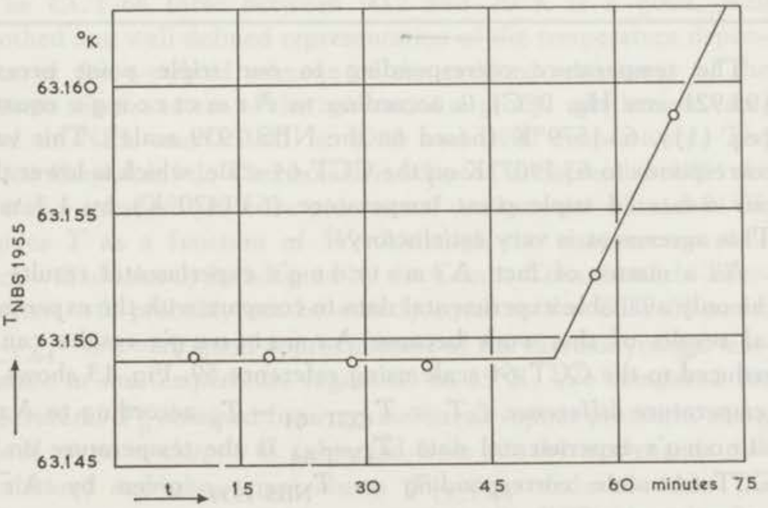

Fig. 12. The temperature $T_{NBS\text{-}1955}$ vs time, showing the constancy of the temperature during one of the triple point measurements.

constancy of the temperature during one of the triple point measurements.

The mean value for the triple point pressure of nitrogen in this experiment is 93.921 mm Hg at 0°C and standard gravity ($g = 980.665$ cm/s^2). It is in good agreement with the average of the values for the triple point pressure measured at different institutes (93.90 mm Hg, 0°C), see table X.

TABLE X

The triple point pressure of nitrogen reported by different authors.

Observers	Year	Reported pressure in mm Hg, 0°C
Verschoyle[61]	1931	93.60
Justi[62]	1931	93.91 ± 0.05
Giauque and Clayton	1933	94.01 ± 0.05
Keesom and Bijl	1937	94.01 ± 0.05
Kirshenbaum and Urey[63]	1942	93.86 ± 0.02
Clusius and Schleich[64]	1958	94.01 ± 0.02
Average		93.90 mm Hg, 0°C

The temperature corresponding to our triple point pressure (93.921 mm Hg, 0°C) is according to Armstrong's equation (eq. (1)), 63.1579°K (based on the NBS-1939 scale). This value corresponds to 63.1407°K on the CCT-64 scale, which is lower than our measured triple point temperature (63.1420°K) by 1.3 m°K. This agreement is very satisfactory.

As a matter of fact, Armstrong's experimental results are the only available experimental data to compare with the experimental results of this work because Armstrong's results can be reduced to the CCT-64 scale using reference 59. Fig. 13 shows the temperature difference $\triangle T = T_{\text{CCT-64}} - T_{\text{p}}$ according to Armstrong's experimental data. $T_{\text{CCT-64}}$ is the temperature on the CCT-64 scale corresponding to $T_{\text{NBS-1939}}$, given by Armstrong, and T_{p} is the temperature obtained from pressure values given by Armstrong using table II, chapter II.

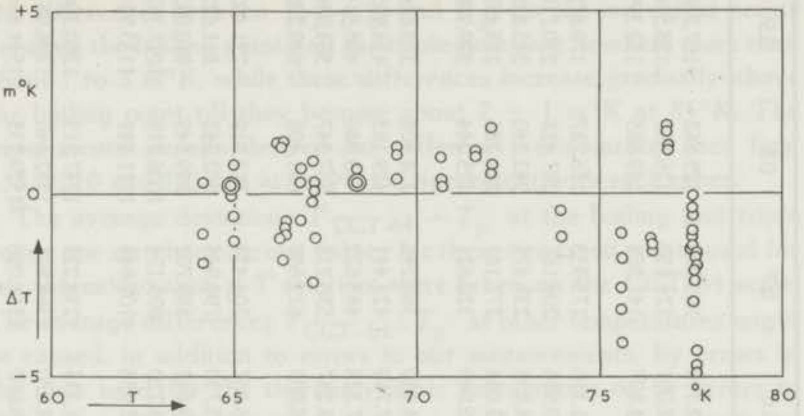

Fig. 13. Differences between temperatures $T_{\mathrm{CCT\text{-}64}}$ on the CCT-64 scale and temperatures T_p obtained from table II, chapter II, according to Armstrong's experimental data. $\Delta T = T_{\mathrm{CCT\text{-}64}} - T_p$.

9. Discussion of the results

a. $T_{\mathrm{CCT\text{-}64}} - T_p$

The CCT-64 table between 90.2 and 20°K is a good, well smoothed and well defined representation of the temperature dependence of the weighted average of the reduced resistances of the platinum thermometers of the international group, which were compared at NPL and PRMI in 1962 and 1963 respectively. The Comité Consultatif de Thermométrie adopted in September 1964 the table as a standard table for provisional use between 12 and 91°K. It gives T as a function of W. Although the temperature scale which will ultimately be adopted by the Comité Consultatif de Thermométrie will probably not be exactly equal to the CCT-64 scale, $T_{\mathrm{CCT\text{-}64}}$ is a very good approximation of the thermodynamic temperature in the temperature region 63 to 85°K. We compared the temperatures T_p obtained from our measured vapour pressures using table II given in chapter II (obtained from our thermodynamic p-T calculation) and the temperatures $T_{\mathrm{CCT\text{-}64}}$ deduced from the resistance measurements and expressed in the CCT-64 scale. According to tables III, IV, V, VI and VII and figs. 7, 8, 9, 10, and 11

TABLE XI

The pressure of the saturated vapour of liquid nitrogen as a smooth function of $T_{\text{CCT-64}}$ according to eq. (10) from 63 up to 85°K. p is expressed in mm Hg at 0° C and standard gravity.

T °K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
63	91.495	93.199	94.929	96.685	98.467	100.275	102.110	103.973	105.862	107.780
64	109.725	111.699	113.701	115.732	117.792	119.881	122.001	124.150	126.330	128.540
65	130.781	133.054	135.358	137.694	140.063	142.464	144.897	147.364	149.865	152.399
66	154.968	157.571	160.209	162.882	165.591	168.335	171.116	173.933	176.787	179.678
67	182.606	185.573	188.578	191.621	194.703	197.825	200.986	204.187	207.428	210.710
68	214.034	217.398	220.804	224.253	227.744	231.278	234.855	238.475	242.140	245.849
69	249.602	253.401	257.245	261.135	265.071	269.054	273.084	277.161	281.286	285.458
70	289.680	293.950	298.270	302.639	307.058	311.528	316.049	320.621	325.244	329.920
71	334.648	339.429	344.263	349.150	354.092	359.088	364.140	369.246	374.408	379.626
72	384.901	390.233	395.622	401.068	406.573	412.137	417.759	423.441	429.183	434.985
73	440.847	446.771	452.757	458.804	464.914	471.087	477.323	483.622	489.986	496.414
74	502.908	509.466	516.091	522.782	529.540	536.365	543.257	550.218	557.247	564.346
75	571.513	578.751	586.059	593.437	600.887	608.409	616.002	623.669	631.408	639.221
76	647.107	655.069	663.105	671.216	679.403	687.667	696.007	704.424	712.919	721.492
77	730.144	738.875	747.685	756.575	765.546	774.597	783.730	792.945	802.242	811.622
78	821.086	830.633	840.264	849.980	859.782	869.669	879.642	889.702	899.849	910.083
79	920.406	930.818	941.318	951.908	962.588	973.359	984.220	995.174	1006.219	1017.357
80	1028.587	1039.912	1051.330	1062.843	1074.450	1086.154	1097.953	1109.849	1121.841	1133.931
81	1146.120	1158.406	1170.792	1183.277	1195.862	1208.548	1221.335	1234.223	1247.213	1260.306
82	1273.502	1286.801	1300.205	1313.713	1327.326	1341.045	1354.870	1368.801	1382.840	1396.987
83	1411.241	1425.604	1440.077	1454.659	1469.352	1484.155	1499.070	1514.096	1529.235	1544.486
84	1559.852	1575.331	1590.924	1606.632	1622.456	1638.396	1654.453	1670.626	1686.918	1703.327
85	1719.855	1736.502	1753.269	1770.157	1787.165	1804.294	1821.546	1838.919	1856.416	1874.036

the differences between $T_{\mathrm{CCT-64}}$ and T_{p} for the individual points between the boiling point and the triple point are nowhere more than about 1 to 3 m°K, while these differences increase gradually above the boiling point till they become about 7 ± 1 m°K at 85°K. The experimental results derived for different thermometers (see figs. 7, 8, 9, 10 and 11) are in very good agreement with each other.

The average deviations $T_{\mathrm{CCT-64}} - T_{\mathrm{p}}$ at the boiling and triple points are zero because our values for these two fixed points used for our thermodynamic p-T relation, were taken on the CCT-64 scale. The average differences $T_{\mathrm{CCT-64}} - T_{\mathrm{p}}$ at other temperatures might be caused, in addition to errors in our measurements, by errors in the data used for the thermodynamic calculations or by errors in $T_{\mathrm{CCT-64}}$. The systematic deviation could be reduced practically to zero if we change the adopted second virial coefficient a little, which can be done within the accuracy of the available data for B. In fact, we used a slightly different method which will be given below.

b. The saturated vapour pressure of liquid nitrogen as a function of $T_{\mathrm{CCT-64}}$

The thermometers T_4 and LN1137601 were used in all measurements while the other thermometers NPL153371, NPL153373 and NBS1575702 were used only in a part of the measurements as can be seen in section 8. It is clear that the spread of the points measured with the thermometer T_4 (see fig. 7) is much smaller than that for the thermometer LN1137601 (see fig. 8). Also, the reproducibility of LN1137601 at the boiling and triple points is within 2.2 and 1.2 m°K respectively, while thermometer T_4 reproduced its temperature indication within 0.2 m°K at both points (see tables VIII and IX). The irreproducibilities for thermometer LN1137601 did not only appear in the nitrogen range but also in the oxygen, the hydrogen and helium ranges in which measurements were carried out with this thermometer in our laboratory. Therefore, we prefer the results deduced from measurements with the thermometer T_4.

The measured pressure as a function of $T_{\mathrm{CCT-64}}$ was represented, using a least squares analysis, by the following equation:

$$^{10}\log p = C_0 + C_1 T + C_2\, {}^{10}\log T + C_3 T^{-1} + \\ + C_4 T^{-2} + C_5 T^{-3} \qquad (10)$$

where p is in mm Hg at 0°C and standard gravity, and T is in °K.

This representation was calculated, firstly for all the measured pressure values and the corresponding $T_{CCT\text{-}64}$ values obtained with the five thermometers (120 pairs of p and T) and secondly excluding the results obtained with the thermometer LN1137601 (40 pairs of p and T). In both representations the measured points for the triple point with thermometers T_4 and LN1137601 were used and were given higher weight. At every measured point the deviation from the representation $\triangle p$ and the corresponding $\triangle T$, were calculated. This was done for the first and the second representation. The deviations $\triangle T$ were presented as a function of T for each thermometer according to both representations. They agree reasonably well although the first representation shows a small systematic deviation. The standard and maximum deviations for the first and second representation are 0.9 and 2.8 m°K, and 0.6 and 2.7 m°K respectively. Further, the first representation gives for the boiling point of nitrogen the value 77.3386°K, while the second gives the value 77.3384°K. Each of these two values is in excellent agreement with the value 77.3385°K given in table VIII. The first and second representation give the same value (63.1418°K) for the triple point temperature corresponding to our measured triple point pressure (93.921 mm Hg, 0°C). This value (63.1418°K) is in good agreement with the value 63.1420°K deduced in table IX. We preferred the second representation. The coefficients of eq. (10) according to the second representation are:

$$
\begin{aligned}
C_0 &= + 0.704645272823 \text{ x } 10^{+1}\\
C_1 &= + 0.124567060037 \text{ x } 10^{-1}\\
C_2 &= - 0.152117492928 \text{ x } 10^{+1}\\
C_3 &= - 0.311954320922 \text{ x } 10^{+2}\\
C_4 &= - 0.137867360621 \text{ x } 10^{+5}\\
C_5 &= + 0.209052236425 \text{ x } 10^{+6}.
\end{aligned}
$$

In fact we tried the least squares representation * using different numbers of negative powers (2, 3 or 4). The accuracies of the representations with 3 and 4 negative powers are nearly the same, but the representation with 2 negative powers shows systematic devia-

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* All these calculations were done for us by Mr. J. A. Dorrepaal at the Mathematical Institute of the University of Leiden.

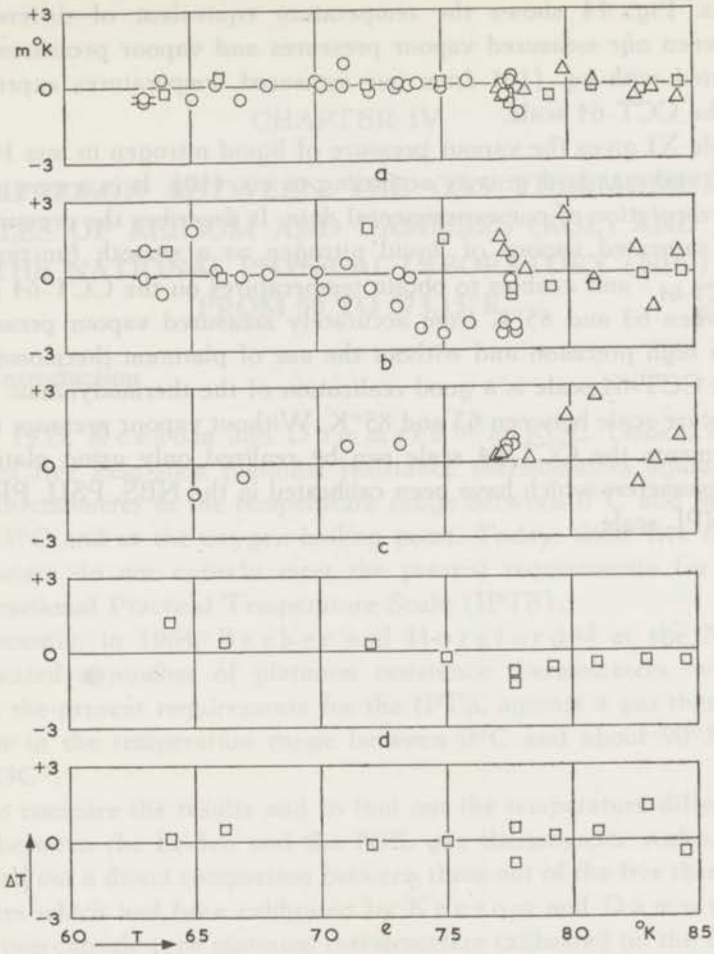

Fig. 14. Differences between temperatures on the CCT-64 scale, deduced from measurements with platinum thermometers, and temperatures deduced from the measured vapour pressures using table XI.

$$\Delta T = T_{\text{CCT-64}} - T_{\text{p (table XI)}}.$$

a. Thermometer T_4
b. Thermometer LN1137601
c. Thermometer NPL153371
d. Thermometer NPL153373
e. Thermometer NBS1575702

tions. Fig. 14 shows the temperature equivalent of differences between our measured vapour pressures and vapour pressures calculated with eq. (10) from our measured temperatures expressed in the CCT-64 scale.

Table XI gives the vapour pressure of liquid nitrogen in mm Hg at 0°C and standard gravity according to eq. (10). It is a very good representation of our experimental data. It describes the pressure of the saturated vapour of liquid nitrogen as a smooth function of $T_{\text{CCT-64}}$ and enables to obtain temperatures on the CCT-64 scale between 63 and 85°K from accurately measured vapour pressures with high precision and without the use of platinum thermometers. The CCT-64 scale is a good realization of the thermodynamic temperature scale between 63 and 85°K. Without vapour pressure measurements the CCT-64 scale can be realized only using platinum thermometers which have been calibrated in the NBS, PSU, PRMI, or NPL scale.

CHAPTER IV

COMPARISON BETWEEN THE GAS THERMOMETER SCALES OF KEESOM AND DAMMERS (KOL) AND OF THE NATIONAL PHYSICAL LABORATORY (NPL) FROM 90 TO 273.15°K

1. Introduction

In 1935, Keesom and Dammers[10] at KOL, Leiden, calibrated five long-stem platinum resistance thermometers against a gas thermometer in the temperature range between 0°C and about —153°C and at the oxygen boiling point. Today, these five thermometers do not entirely meet the present requirements for the International Practical Temperature Scale (IPTS).

Recently, in 1964, Barber and Horsford[12] at the NPL calibrated a number of platinum resistance thermometers, which meet the present requirements for the IPTS, against a gas thermometer in the temperature range between 0°C and about 90°K or —183C°.

To compare the results and to find out the temperature differences between the Leiden and the NPL gas thermometer scales, we carried out a direct comparison between three out of the five thermometers which had been calibrated by Keesom and Dammers, and two capsule-type platinum thermometers calibrated on the NPL scale in the temperature range between 10 and 273.15°K. These five thermometers were compared between about 64 and 273.15°K. For this purpose we designed and constructed an apparatus for maintaining a constant-temperature bath for use in the considered temperature region. It is in principle similar to that described by Scott and Brickwedde[65]. In the considered temperature range, the temperature can be easily adjusted to any desired value and can be maintained constant for a long time. The constant-temperature bath is contained in a double walled glass dewar which is surrounded by an outer glass dewar partly filled with liquid nitrogen for refrigeration. The refrigeration was controlled by keeping the nitrogen level in the outer dewar constant and by varying the gas pressure between the walls of the inner dewar. The liquid in the inner dewar is circulated by a vane in the bottom of a stainless steel tube, which has four openings in its upper part and is centrally located in the inner dewar vessel. When stirred the liquid rises inside of the stainless steel tube and flows down on the outside. The inside of the stainless steel tube is the constant-temperature region of the cryostat. For the temperature region from 0°C down to —140°C liquid isopentane has been used for the bath liquid. For temperatures between —125 and —183°C liquid propane has been used, while for still lower temperatures liquid oxygen or nitrogen has been used.

2. **Apparatus**

The apparatus is shown in fig. 1. The inner dewar D_1 (57 × 10.8 cm) is connected to the cap of the cryostat by a rubber seal. The space between the two walls of D_1 is connected to a mercury diffusion pump, McLeod gauge and helium cylinder by means of tube T_1. The outer dewar D_2 surrounds the inner dewar and is supported from below on a pedestal.

The cylinder *M* (50 × 9 cm) is not made entirely of stainless steel but the upper part consists of pertinax. Both parts are connected to each other by means of small screws and supported by a brass ring R_1 which is fastened at the cap of the cryostat (see fig. 1). The pertinax has been used to reduce the heat influx by conduction from the top of the cryostat to the bath. *M* has the piece *V* at its bottom to provide good circulation of the liquid. The four openings *W* (2.5 × 6 cm) were cut partly into the upper end of the stainless steel tube and partly into the lower end of the pertinax tube (see fig. 1). Below the four openings *W*, *M* is wrapped in a silicon impregnated fibre glass sheet on which the heating coil H_1, shown by the dots, is wound tightly to keep the wire from slipping and to separate the heater coil from the stirring tube *M*. The heater coil H_1 is made of constantan wire and has a resistance of about 35 Ω. Distributing the heater over a large surface instead of concentrating it in a small part of the bath prevents the occurrence of hot spots in the cryostat. It is advantageous in compensating for an

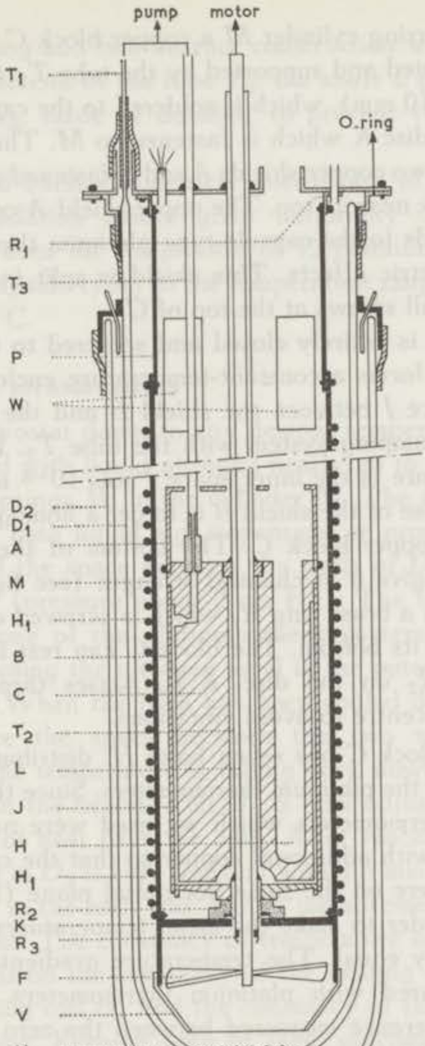

Fig. 1. Apparatus for comparison of platinum resistance thermometers in the temperature range from 63 up to 273.15°K.

excess of refrigeration, over that needed to maintain a desired temperature, to have the heating surface close to and distributed over the refrigerating surface.

Inside the stirring cylinder *M* a copper block *C* (75 × 170 mm) is centrally located and supported by the tube T_2 (stainless steel of inner diameter 10 mm), which is soldered to the cap of the cryostat. *C* rests on the disc *K* which is fastened to *M*. The copper block is surrounded by two copper shields *A* and *B* fastened at the cylindrical side of the block near its top. The upper shield *A* covers the connections of the leads to the capsule-type platinum thermometers to reduce thermoelectric effects. This shield is split in two halves and fastened by small screws at the top of *C*.

The shield *B* is entirely closed and soldered to the copper block near its top. It forms a constant-temperature enclosure around the block. The space *J* between the shield *B* and the block *C* is connected to the pumping system with the tube T_3. During measurements the pressure in the inner space *J* was 10^{-5} mm Hg or lower. The main purpose of the shield *B* is to get a homogeneous temperature over the copper block *C*. The bottom of the shield *B* has a special form to give it mechanical strength (see fig. 1). Below the shield *B* there is a brass ring R_2 which is screwed onto the tube T_2 and soldered at its bottom. The block *C* can rest in a smooth way by means of R_2 on the disc. $K.T_2$ passes through a hole in *K* precisely at the centre to avoid vibrations.

The copper block *C* has seven holes *H*, distributed in a suitable way, for placing the platinum thermometers. Since the dimensions of the platinum thermometers which we used were not the same, we filled the holes with additional copper so that the centres of all the thermometers were on the same horizontal plane (let us call it the zero level) in order to make the mean temperatures of the thermometers accurately equal. The temperature gradient in the block *C* has been measured with platinum thermometers. The maximum temperature difference measured between the zero level and 4 cm above the zero level is less than 1 m°K.

During stirring the liquid level in the inner bath is kept below the top of the openings *W* to reduce the heat input from above. The vane *F* is driven at a speed of about 500 revolutions per minute by means of the shaft *L* (stainless steel tube of inner diameter 4 mm) which is connected through a flexible shaft to a motor outside the cryostat. The shaft *L* is centrally located in the tube T_2. Outside the cryostat the shaft *L* and the tube T_2 are connected to each other by means of an O-ring and ball-bearing construction which is vacuum tight. At the lower end of the tube T_2, the shaft L passes precisely through a ring R_3, made of dehalite, to prevent vibration during stirring.

A stirred liquid bath, symmetrical distribution of the parts, and suitable heat insulation assure great uniformity of temperature. This appartus is used for comparison of 13 platinum thermometers (long-stem and capsule-type) in the temperature range between 0°C and about –210°C.

3. Procedure of measurements

To cool the cryostat down to any desired temperature the outer dewar D_2 is filled with liquid nitrogen nearly up to the level of the bottom of the openings W in the cylinder M. The inner dewar D_1 is filled with the bath liquid *e.g.* isopentane or propane. Once the stirring is started the space between the walls of D_1 is filled with some helium gas (pressure about 2 cm Hg). The temperature fall is observed by one of the platinum thermometers in the copper block. During cooling the nitrogen level in the outer dewar is kept nearly constant. When the bath has been cooled down to the desired temperature the space between the two walls of D_1 is evacuated until the temperature is falling very slowly. The heating current flowing in the heating coil H_1 is now adjusted to compensate for the loss of heat from the bath. After reaching equilibrium, the nitrogen level in D_2 is kept constant within 5 mm. The maximum temperature drift in the bath was, during measurements, within ± 2 to 3 m°K per hour. The constancy of temperature in the bath for a long time depends on the constancy of the heating current flowing through the heating coil H_1 and the constancy of the nitrogen level in the outer dewar. Keeping both of them precisely constant, the cryostat temperature stays constant for a long time within 1 m°K.

To bring the bath to a higher temperature a higher current is sent through the heating coil H_1. When the desired temperature is reached the heating current is adjusted to compensate for the loss of heat.

The temperature gradient in the copper block is practically zero. To test the uniformity of temperature, one of the platinum resistance thermometers (long-stem) which is immersed in the copper block was measured at different heights. By comparing it with the standard thermometer NPL153371 which remains in its place, the maximum temperature difference measured at 4 cm above the zero level is less than one millidegree.

For measurements in the temperature range from about 90 down to about 64°K, a bath of liquid oxygen or nitrogen was used. To realize a desired lower temperature, the pressure over the bath is reduced and adjusted to the desired value. Reaching the desired pressure value the cryostat pressure is kept constant using a cartesean manostat. When we used a liquid oxygen or nitrogen bath, the heater H_2 at the bottom of the inner dewar D_1 was used. To bring the bath to a higher temperature a heating current is sent through the heater H_2. Arriving at the desired temperature the current is reduced to about 100 mA and the cryostat pressure is kept constant. More details concerning temperature measurements in this range (90 to 64°K) are given in chapter III.

With the isopentane bath we covered the temperature range from 0°C down to about –132°C, and with propane the range from about –121.5°C down to about –183°C. In the common temperature range, between –121 and –132°C, measurements were made with both liquids (isopentane and propane), which served as a check for the reproducibility of the measurements. Between 0 and –183°C measurements at about every 10°C were made, while in the range from about 90°K down to 64°K at about every 3°K.

When the temperature drift in the constant-temperature bath became negligible, a series of measurements was carried out for about 80 minutes. In these measurements we chose the thermometer NPL153371 as a standard thermometer representing the NPL scale. This thermometer has been compared with the others (Pt 68, 70, 71 and NPL164956) alternatively at each measured temperature. The measuring current (thermometer current) in all measurements was 1 mA. The measurements can be divided into four series as indicated in section 5.

4. Platinum thermometers

The experiment was carried out using five platinum thermometers. Two of them are of the capsule-type ,manufactured by Tinsley and calibrated on the NPL scale. The other three are long-stem thermometers, made by Keesom and Dammers and were calibrated with their helium gas thermometer at the KOL in 1935.

a. NPL thermometers

The NPL thermometers have the identification nos. 153371 and 164956. Both of them are calibrated on the NPL scale in the range from 10 up to 273.15°K by comparison with a platinum resistance thermometer which had been compared with a helium gas thermometer. The reference temperature of the NPL scale is the boiling point of oxygen with a value of 90.18°K which corresponds in the IPTS to the value −182.97°C when the thermodynamic temperature of the ice point is taken as 273.15°K. These two thermometers nos. 153371 and 164956 were calibrated in the range from 10 to 90°K in 1961 and 1962 respectively, and from 90 to 273.15°K in 1965. Both of them meet the present requirements for the IPTS. For the present work NPL153371 has been used as a standard thermometer. Some of the basic data are given in table I.

TABLE I

Ice point and steam point data for thermometer NPL153371 according to our measurements.

Date	15.6.62	18.6.62	25.6.62	26.6.62	28.6.62
$R(0°\mathrm{C})$ Ω	25.37789	25.37790	25.37805	25.37797	25.37799
Date	18.4.64	16.12.64	20.3.65	17.11.65	23.11.65
$R(0°\mathrm{C})$ Ω	25.37788	25.37793	25.37805	25.37802	25.37797
Date	20.6.62	27.6.62	22.11.65		
$R(100°\mathrm{C})/R(0°\mathrm{C})$	1.392638	1.392635	1.392639		

Mean values

$R(0°\mathrm{C}) = 25.37797\ \Omega$

$R(100°\mathrm{C})/R(0°\mathrm{C}) = 1.392637^{3}$

$10^{3}\alpha = 3.92637^{3}$

b. Keesom and Dammers thermometers (Leiden thermometers)

Leiden thermometers used in our experiments have the identification numbers 68, 70 and 71. The specification of these thermometers are:

1. Pt 68 made of wire from Heraeus, Sample I, 0.1 mm in diameter, on a porcelain tube.

2. Pt 70 made of wire from the National Bureau of Standards (USA), 0.2 mm in diameter, on a porcelain tube.

3. Pt 71 made of wire from Heraeus, Sample I, 0.1 mm in diameter, on a porcelain tube.

These thermometers had been constructed in the Kamerlingh Onnes Laboratory and were calibrated in the temperature range from 0 down to –153°C and at –182.983°C, by Keeson and Dammers. They were calibrated with a helium gas thermometer using the ice point as a reference temperature and taking the absolute temperature of the ice point equal to 273.144°K. Keesom and Dammers recommended as the best value for the oxygen boiling point –182.983°C; this corresponds to 90.161°K in their Kelvin scale.

c. **Redetermination of the basic points of the Leiden thermometers**

We cleaned the thermometers Pt 68, 70 and 71 in boiling distilled water and remounted them in new glass envelopes. They were filled with helium gas (20 cm Hg) and sealed off. The thermometers were repeatedly cooled in liquid nitrogen for a few hours. The resistance at the oxygen, ice and steam points were measured alternatively for the three thermometers, to check their reproducibilities and to find out the changes in the thermometers since 1935. For all measurements a measuring current of 1 mA has been used.

The reduced resistances at the steam point, the ice point and the oxygen boiling point for the thermometers Pt 68, 70 and 71 are given in tables II, III and IV. The reduced resistances of the thermometers at the boiling point of oxygen were obtained from comparisons with the thermometer NPL153371 for which $W(O_2) = 0.243815$ according to the calibration at NPL. The actual comparisons were not made exactly at the boiling point but in the neighbourhood of it. The data were recalculated to the boiling point using the relation

$$W_x\,(O_2) = W_x(T_m) - (\alpha_x/\alpha_s)\left\{W_s(T_m) - W_s(O_2)\right\} \qquad (2)$$

where

$W_x(O_2)$ is the reduced resistance of the thermometer Pt 68, 70 or 71 at the boiling point of oxygen

TABLE II

Some of the basic data of Pt 68 according to the present work and the corresponding values given by Keesom and Dammers.

Date	$R(0°C)$ Ω	Date	$R(100°C)/R(0°C)$	$10^3\alpha$ °C^{-1}	Date	$R(O_2)/R(0°C)$
6.3.65	12.45621	9.3.65	1.391063	3.91063	15.4.65	0.246666
11.3.65	12.45593	5.4.65	1.391060	3.91060	15.4.65	0.246664
8.4.65	12.45589				5.5.65	0.246663
14.8.65	12.45588				6.5.65	0.246663
Mean values	12.45589		1.391061^5	3.91061^5		0.246664
Dammers values			1.391178^7	3.91178^7		0.246519^4

TABLE III

Some of the basic data of Pt 70 according to the present work and the corresponding values given by Keesom and Dammers.

Date	$R(0°C)$ Ω	Date	$R(100°C)/R(0°C)$	$10^3\alpha$ °C^{-1}	Date	$R(O_2)/R(0°C)$
6. 3.65	3.429538	9.3.65	1.391479	3.91479	15.4.65	0.245904
11. 3.65	3.429547	5.4.65	1.391488	3.91488	15.4.65	0.245907
8. 4.65	3.429587				5.5.65	0.245906
15.10.65	3.429536				6.5.65	0.245906
18.10.65	3.429510					
Mean values	3.42954		1.391483^5	3.91483^5		0.245905^8
Dammers values			1.391454^6	3.91454^6		0.245847^3

TABLE IV

Some of the basic data of Pt 71 according to the present work and the corresponding values given by Keesom and Dammers.

Date	$R(0°C)$ Ω	Date	$R(100°C)/R(0°C)$	$10^3\alpha$ °C^{-1}	Date	$R(O_2)/R(0°C)$
10.10.64	12.50620	13.10.64	1.391434	3.91434	15.4.65	0.246114
20.10.64	12.50624	9. 3.65	1.391436	3.91436	15.4.65	0.246116
28.10.64	12.50620	15.10.65	1.391435	3.91435	5.5.65	0.246106
25.12.64	12.50618				6.5.65	0.246108
6. 3.65	12.50620					
11. 3.65	12.50616					
15.10.65	12.50619					
18.10.65	12.50633					
Mean values	12.50621		1.391435	3.91435		0.246111
Dammers values			1.391386^5	3.91386^5		0.246068^0

$W_x(T_m)$ is the measured reduced resistance, in the neighbourhood of the oxygen boiling point, of the thermometer Pt 68, 70 or 71

α_x is the temperature coefficient of the thermometer Pt 68, 70 or 71

α_s is the temperature coefficient of the thermometer NPL153371

$W_s(T_m)$ is the measured reduced resistance, in the neighbourhood of the boiling point of oxygen, of the thermometer NPL153371

W_s (O_2) is the reduced resistance of the thermometer NPL153371 at the boiling point of oxygen (90.18°K).

Eq. (2) holds exactly if Matthiessen's rule is valid, but it can be used with sufficient accuracy here because $T_m - T_{O_2}$ is smal..

d. The changes of the thermometers Pt 68, 70 and 71 since 1935

1. Oxygen boiling point

According to the gas thermometer measurements of Keesom and Dammers, the temperature of the boiling point of oxygen is –182.985°C. This value corresponds to 90.159°K on the thermodynamic scale where the thermodynamic temperature of the ice point is 273.144°K, the value used by Keesom and Dammers. Recalculating the value –182.985°C according to the recommended value 273.15°K for the temperature of the ice point, we get —182.989°C $\{= 273.15—(273.15/273.144)90.159\}$. That is to say, the reduced resistance $W(O_2)$ values given by Keesom and Dammers were in fact W^{1935} (—182.989°C) values where 1935 refers to the year in which Keesom and Dammers made their measurements.

We assumed that the gas thermometer scale of Keesom and Dammers at –183°C is equal to the gas thermometer scale of NPL. Admitting that this assumption is somewhat arbitrary we are able to find the change in the thermometers at the boiling point of oxygen. By adding to the reduced resistance W^{1935} (—182.989°C) measured by Keesom and Dammers, the increase in W for 19.0 m°K, we obtain

$$W^{1935}(—182.970°\mathrm{C}) = W^{1935}(—182.989°\mathrm{C}) + \\ + 0.0190(\mathrm{d}W/\mathrm{d}t)_{O_2}.$$

In tables II, III and IV our data for W at the oxygen boiling point, $t = -182.970^\circ C$ according to the NPL scale, are given. If these are denoted by $W^{1965}(-182.970^\circ C)$, the change in the thermometers between 1935 and 1965 is

$$\triangle W(O_2) = W^{1965}(-182.970^\circ C) - W^{1935}(-182.970^\circ C).$$

Table V gives the values of the reduced resistance for Pt 68, 70 and 71, at the oxygen boiling point 90.180°K or –182.970°C according to the measurements of the present work and of Keesom and Dammers.

TABLE V

The $W(-182.970^\circ C)$ values for Keesom and Dammers thermometers Pt 68, 70 and 71 according to their measurements in 1935 and the present work in 1965.

Year	$W(-182.970^\circ C)$		
	Pt 68	Pt 70	Pt 71
1965 (present work)	0.246664^2	0.245905^8	0.246111^2
1935 (according to K&D values)	0.246601^9	0.245929^8	0.246150^5
$\triangle W(O_2)$	0.000062^3	-0.000024^0	-0.000039_3

2. Steam point

From the measurements at the steam point by Keesom and Dammers in 1935 and the present work, the reduced resistance difference at the steam point, $\triangle W(100^\circ C) = W^{1965}(100^\circ C) - W^{1935}(100^\circ C)$, can be obtained directly. Table VI gives

TABLE VI

The reduced resistance $W(100^\circ C)$ at the steam point for the thermometers Pt 68, 70 and 71, according to measurements in 1935 and 1965 and the difference $\triangle W(100^\circ C) = W^{1965}(100^\circ C) - W^{1935}(100^\circ C)$.

Year	$W(100^\circ C)$		
	Pt 68	Pt 70	Pt 71
1965 (present work)	1.391061^5	1.391483^5	1.391435^2
1935 (K&D values)	1.391178^7	1.391454^6	1.391386^5
$\triangle W(100^\circ C)$	-0.000117^2	0.000028^9	0.000048^7

$W(100°C)$ values for the thermometers Pt 68, 70 and 71 in 1965 and 1935 and the differences $\triangle W(100°C)$.

3. Applied corrections

It is clear from tables V and VI that the reduced resistances of the thermometers Pt 68, 70 and 71 changed at the oxygen boiling point and at the steam point. Pt 68 changed considerably because this thermometer has been used frequently in our laboratory and unfortunately has been broken and repaired more than once. To account for the changes in the thermometers Pt 68, 70 and 71 from 1935 to 1965, we applied corrections as follows.

The changes $\triangle W$ in the reduced resistances at the steam point and the oxygen point are taken from tables VI and V respectively. At the ice point the change is of course zero. At other temperatures $\triangle W^*$ was calculated from $\triangle W(100°C)$, $\triangle W(0°C) = 0$ and $\triangle W\ (O_2)$ using the relation

$$\triangle W^* = c_1 t + c_2 t^3\ (t - 100).$$

Figs. 2, 3 and 4 show the corrections $\triangle W^*$, as functions of t, which have been applied for the thermometers Pt 68, 70 and 71 respectively.

5. Experimental results

When equilibrium had been realized at a desired temperature a series of measurements was carried out during an interval of about 70 to 80 minutes. The resistances of the thermometers Pt 68, 70, 71 and NPL164956 were compared with that of the thermometer NPL153371. From the measured reduced resistance values W_{153371} the corresponding temperatures were calculated using its calibration tables. From the measured reduced resistances W_x (x means Pt 68, 70, 71 and NPL164956) and the corresponding W_{153371}, the temperature dependence of the reduced resistance differences $\triangle W_{exp} (= W_x - W_{153371})$ as functions of temperature are obtained. The experimental data are given in tables VII, VIII and IX. These $\triangle W_{exp}$ values for each thermometer have been plotted in a graph as a function of T_{153371} in the temperature range from 64 to 273.15°K. Smooth curves were drawn through the experimental points. $\triangle W_{exp}$ is nearly a linear function of temperature for temperatures between 0 and —183°C and can be approximated by the expression

$$10^6 \triangle W_{\text{calc}} = c(T - 273.15°\text{K}). \tag{3}$$

The average of the $\triangle W_{\text{exp}}$ values at the oxygen boiling point for

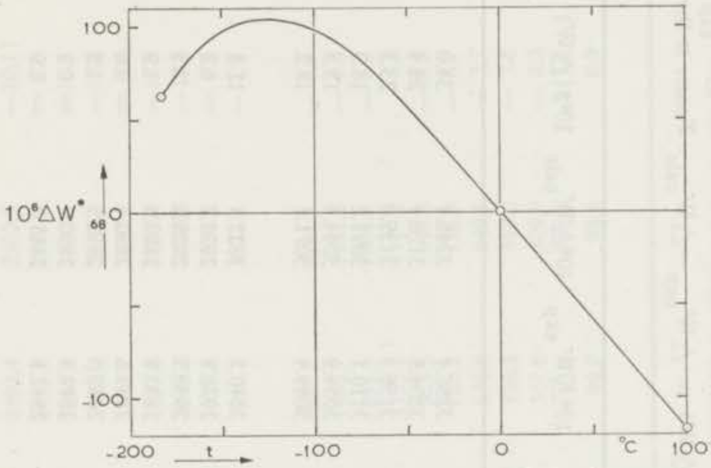

Fig. 2. The change $\triangle W^*$ in the reduced resistance of the thermometer Pt 68 since 1935. $\triangle W^* = -1.172\, t\, 10^{-6} - 0.87773\; t^3(t-100)\,10^{-13}$.

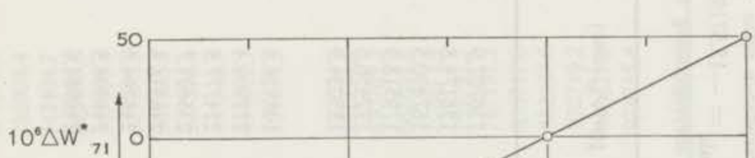

Fig. 3. The change $\triangle W^*$ in the reduced resistance of the thermometer Pt 70 since 1935. $\triangle W^* = 0.289\, t\, 10^{-6} + 0.16673\; t^3(t-100)\,10^{-13}$.

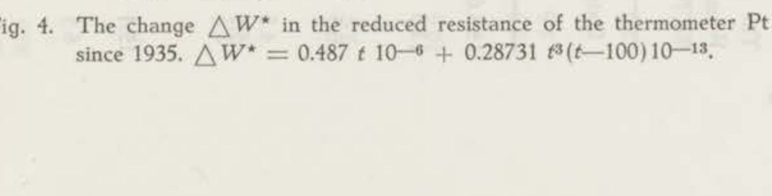

Fig. 4. The change $\triangle W^*$ in the reduced resistance of the thermometer Pt 71 since 1935. $\triangle W^* = 0.487\, t\, 10^{-6} + 0.28731\; t^3(t-100)\,10^{-13}$.

TABLE VII

The measured resistance ratio $W = R(T)/R(273.15°\mathrm{K})$ for thermometers Pt 68 and NPL153371, $\triangle W_{\mathrm{exp}} = W_{68}(^{1965}) - W_{153371}$, $\triangle W_{\mathrm{calc}} = -15.571951\ (T - 273.15°\mathrm{K})10^{-6}$ and $\delta(\triangle W) = \triangle W_{\mathrm{exp}} - \triangle W_{\mathrm{calc}}$. T_{153371} is the temperature, on the NPL scale, corresponding to W_{153371}.

Date	$10^6 W_{68}(^{1965})$	$10^6 W_{153371}$	T_{153371} °K	$10^6 \triangle W_{\mathrm{exp}}$	$10^6 \triangle W_{\mathrm{calc}}$	$10^6 \delta(\triangle W)$	Bath liquid
14.5.65	136707.9	133421.5	64.5432	3286.4	3248.4	38.0	N_2
	156174.8	152970.0	69.1669	3204.8	3176.4	28.4	
13.5	167490.5	164332.2	71.8272	3158.3	3135.0	23.3	
	179518.9	176408.8	74.6381	3110.1	3091.2	18.9	
	192456.6	189396.7	77.6456	3059.9	3044.4	15.5	
6.5	185034.9	181945.5	75.9220	3089.4	3071.2	18.2	
4.5	198526.8	195486.5	79.0514	3040.3	3022.5	17.8	O_2
5.5	212909.4	209932.5	82.3790	2976.9	2970.7	6.2	
	224777.5	221847.0	85.1203	2930.5	2928.0	2.5	
	235621.7	232730.8	87.6256	2890.9	2889.0	1.9	
	246316.8	243467.0	90.0998	2849.8	2850.4	— 0.6	
15.4	246294.0	243442.0	90.0940	2852.0	2850.5	1.5	
	246396.5	243547.2	90.1183	2849.3	2850.2	— 0.9	
6.5	246984.6	244137.5	90.2544	2847.1	2848.0	— 0.9	
29.6	276185.4	273446.1	97.0115	2739.3	2742.8	— 3.5	propane
30.6	286909.4	284217.2	99.5008	2692.2	2704.1	—11.9	
	342404.7	339912.3	112.4433	2492.4	2502.5	—10.1	
	342468.6	339973.3	112.4576	2495.3	2502.3	— 7.0	
	397509.4	395225.5	125.4239	2283.9	2300.4	—16.5	
1.7	424978.5	422794.1	131.9397	2184.4	2198.9	—14.5	
	507308.2	505421.5	151.6319	1886.7	1892.3	— 5.6	
	507326.4	505448.8	151.6385	1877.6	1892.2	—14.6	
4.6	463248.7	461202.4	141.0642	2046.3	2056.8	—10.5	
	495042.7	493113.9	148.6843	1928.8	1938.2	— 9.4	
	524646.5	522836.4	155.8108	1810.1	1827.2	—17.1	
9.6	581330.6	579723.5	169.5227	1607.1	1613.7	— 6.6	isopentane
	620765.3	619301.6	179.1139	1463.7	1464.3	— 0.6	
	662689.4	661391.1	189.3565	1298.3	1304.8	— 6.5	
10.6	708673.4	707538.3	200.6345	1135.1	1129.2	5.9	
	755792.7	754867.2	212.2502	925.5	948.3	—22.8	
	797191.2	796411.0	222.4855	780.2	788.9	— 8.7	
2.6	835717.0	835080.6	232.0449	636.4	640.1	— 3.7	
3.6	882337.6	881881.1	243.6551	456.5	459.3	— 2.8	
	920719.2	920411.6	253.2463	307.6	309.9	— 2.3	
	960527.2	960374.4	263.2248	152.8	154.6	— 1.8	
2.6	974785.4	974685.7	266.8060	99.7	98.8	0.9	

TABLE VIII

The measured resistance ratio $W = R(T)/R(273.15°K)$ for thermometers Pt 70 and NPL153371, $\triangle W_{exp} = W_{70}(^{1965})$ — W_{153371}, $\triangle W_{calc} = 11.427009\ (T - 273.15°K)\ 10^{-6}$ and $\delta(\triangle W) = \triangle W_{exp} - \triangle W_{calc}$. T_{153371} is the temperature, on on the NPL scale, corresponding to W_{153371}.

Date	$10^6 W_{70}(^{1965})$	$10^6 W_{153371}$	T_{153371} °K	$10^6 \triangle W_{exp}$	$10^6 \triangle W_{calc}$	$10^6 \delta(\triangle W)$	Bath liquid
14.5.65	135786.9	133433.9	64.5462	2353.0	2383.7	—30.7	N_2
	155268.8	152960.3	69.1646	2308.5	2330.9	—22.4	
13.5	166626.3	164340.1	71.8290	2286.2	2300.5	—14.3	
	178633.4	176379.0	74.6311	2254.4	2268.5	—14.1	
	191612.5	189390.5	77.6441	2222.0	2234.0	—12.0	
6.5	184166.9	181923.6	75.9169	2243.0	2253.8	—10.8	
4.5	197688.2	195484.0	79.0508	2204.2	2218.0	—13.8	O_2
5.5	212103.1	209925.5	82.3774	2177.6	2180.0	— 2.4	
	223979.6	221836.2	85.1178	2143.4	2148.6	— 5.2	
	234854.8	232737.6	87.6272	2117.2	2120.0	— 2.8	
	245531.4	243439.8	90.0936	2091.6	2091.8	— 0.2	
15.4	245528.0	243438.0	90.0930	2090.0	2091.8	— 1.8	
	245636.3	243543.3	90.1174	2093.0	2091.5	1.5	
6.5	246194.9	244104.0	90.2467	2090.9	2090.0	0.9	
29.6	262932.0	260880.4	94.1118	2051.6	2045.9	5.7	propane
30.6	286196.0	284194.9	99.4957	2001.1	1984.3	16.8	
	341786.5	339943.2	112.4505	1843.3	1836.3	7.0	
	396922.6	395228.4	125.4246	1694.2	1688.1	6.1	
1.7	424356.9	422731.6	131.9249	1625.3	1613.8	11.5	
	424459.8	422835.9	131.9496	1623.9	1613.5	10.4	
	506829.5	505429.5	151.6339	1400.0	1388.6	11.4	
4.6	462768.9	461247.8	141.0750	1521.1	1509.2	11.9	isopentane
	494595.2	493163.4	148.6961	1431.8	1422.1	9.7	
	524153.9	522789.6	155.7995	1364.3	1341.0	23.3	
	558294.7	557030.2	164.0418	1264.5	1246.8	17.7	
9.6	580902.5	579708.9	169.5192	1193.6	1184.2	9.4	
	620530.8	619444.7	179.1487	1086.1	1074.2	11.9	
	662379.5	661409.5	189.3610	970.0	957.5	12.5	
10.6	707997.7	707151.1	200.5395	846.6	829.7	16.9	
	755657.0	754954.6	212.2717	702.4	695.7	6.7	
	796146.3	795547.3	222.2724	599.0	581.4	17.6	
2.6	835498.6	835029.1	232.0321	469.5	469.9	— 0.4	
3.6	882248.5	881906.6	243.6614	341.9	337.0	4.9	
	920599.5	920370.0	253.2359	229.5	227.6	1.9	
	960441.2	960323.0	263.2119	118.2	113.6	4.6	
2.6	974783.6	974706.8	266.8113	76.8	72.4	4.4	

TABLE IX

The measured resistance ratio $W = R(T)/R(273.15°\mathrm{K})$ for thermometers Pt 71 and NPL153371, $\triangle W_{\mathrm{exp}} = W_{71}(^{1965}) - W_{153371}$, $\triangle W_{\mathrm{calc}} = -12.549598\ (T - 273.15°\mathrm{K})10^{-6}$ and $\delta(\triangle W) = \triangle W_{\mathrm{exp}} - \triangle W_{\mathrm{calc}}$. T_{153371} is the temperature, on on the NPL scale, corresponding to W_{153371}.

Date	$10^6 W_{71}(^{1965})$	$10^6 W_{153371}$	T_{153371} °K	$10^6 \triangle W_{\mathrm{exp}}$	$10^6 \triangle W_{\mathrm{calc}}$	$10^6 \delta(\triangle W)$	Bath liquid
14.5.65	136120.5	133439.4	64.5475	2681.1	2617.9	63.2	N_2
	155555.6	152948.7	69.1618	2606.9	2560.0	46.9	
13.5	166907.2	164341.4	71.8293	2565.8	2526.5	39.3	
	178893.7	176371.2	74.6293	2522.5	2491.4	31.1	
	191877.5	189400.6	77.6465	2476.9	2453.5	23.4	
6.5	184418.1	181914.5	75.9148	2503.6	2475.2	28.4	
4.5	197928.9	195473.6	79.0484	2455.3	2435.9	19.4	O_2
5.5	212334.2	209925.6	82.3775	2408.6	2394.1	14.5	
	224197.0	221828.0	85.1159	2369.0	2359.8	10.2	
	235063.4	232733.9	87.6263	2329.5	2328.2	1.3	
	245724.2	243431.8	90.0917	2292.4	2297.3	— 4.9	
15.4	245742.0	243440.0	90.0935	2302.0	2297.3	4.7	
	245844.9	243545.1	90.1178	2299.6	2297.0	2.6	
6.5	246384.6	244092.1	90.2439	2292.5	2295.4	— 2.9	
29.6	243903.4	241599.2	89.6690	2304.2	2302.6	1.6	
	262791.4	260555.3	94.0368	2236.1	2247.8	—11.7	propane
	275504.0	273303.6	96.9786	2200.4	2210.9	—10.5	
30.6	286395.2	284232.6	99.5044	2162.6	2179.2	—16.6	
	341872.6	339880.2	112.4358	1992.4	2016.9	—24.5	
	397046.7	395227.3	125.4243	1819.4	1853.9	—34.5	
1.7	424480.6	422746.4	131.9284	1734.2	1772.3	—38.1	
1.7	506944.8	505458.2	151.6407	1486.6	1524.9	38.3	
4.6	462883.9	461266.7	141.0795	1617.2	1657.4	—40.2	isopentane
	494720.2	493196.4	148.7040	1523.8	1561.7	—38.9	
	524288.6	522851.1	155.8143	1437.5	1472.5	—35.0	
	558445.4	557110.4	164.0612	1335.0	1369.0	—34.0	
9.6	581036.0	579761.3	169.5318	1274.7	1300.4	—25.7	
	620633.5	619483.4	179.1581	1150.1	1179.6	—29.5	
	662477.5	661454.5	189.3720	1023.0	1051.4	—28.4	
10.6	708129.4	707244.8	200.5625	884.6	910.9	—26.3	
	755779.3	755030.7	212.2904	748.6	763.8	—15.2	
	796263.0	795640.5	222.2954	622.5	638.2	—15.7	
2.6	835497.9	834997.9	232.0244	500.0	516.1	—16.1	
3.6	882278.9	881915.9	243.6637	363.0	370.0	— 7.0	
	920581.4	920339.3	253.2282	242.1	250.0	— 7.9	
	960439.1	960314.5	263.2098	124.6	124.7	— 0.1	
2.6	974796.6	974712.9	266.8128	83.7	79.5	+ 4.2	

each thermometer were used to calculate the values of the constant *c*. The relations are for the thermometers Pt 68, 70 and 71

$$10^6 \triangle W_{\mathrm{calc}} = -15.57195(T - 273.15°\mathrm{K}) \quad \mathrm{Pt}\ 68 \qquad (4)$$

$$10^6 \triangle W_{\mathrm{calc}} = -11.42700(T - 273.15°\mathrm{K}) \quad \mathrm{Pt}\ 70 \qquad (5)$$

and $$10^6 \triangle W_{\mathrm{calc}} = -12.54959(T - 273.15°\mathrm{K}) \quad \mathrm{Pt}\ 71 \qquad (6)$$

The deviations of the measured $\triangle W_{\mathrm{exp}}$ values fom the corresponding $\triangle W_{\mathrm{calc}}$ values, $\delta(\triangle W) = \triangle W_{\mathrm{exp}} - \triangle W_{\mathrm{calc}}$ are represented in figs. 5, 6 and 7. Smooth curves were drawn through the experimental points. Using figs. 5, 6 and 7 and eqs. (4), (5) and (6), we can calculate the $\triangle W_{\mathrm{exp}}$ values at any desired temperature.

6. Differences between the gas thermometer scales of Keesom and Dammers and of NPL

Five platinum thermometers were calibrated in 1935 by Keesom and Dammers against a gas thermometer. In our experiment a direct comparison between three of the five thermometers and the thermometer NPL153371 has been carried out. To compare the experimental data of Keesom and Dammers with the NPL gas thermometer scale we have to consider that:

a. Due to the changes of the thermometers, see section 4, paragraph *d3*, a correction $\triangle W^*$ taken from figs. 2, 3 and 4 has to be applied

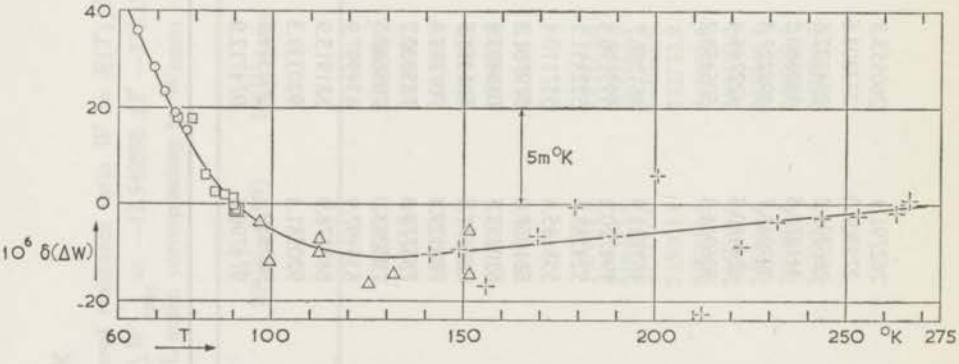

Fig. 5. The deviations of the measured reduced resistance differences $\triangle W_{\mathrm{exp}}$ ($= W_{68} - W_{153371}$) values from a linear relation $\triangle W_{\mathrm{calc}} = -15.57195\ (T - 273.15°\mathrm{K}) 10^{-6}$. $\delta(\triangle W) = \triangle W_{\mathrm{exp}} - \triangle W_{\mathrm{calc}}$.

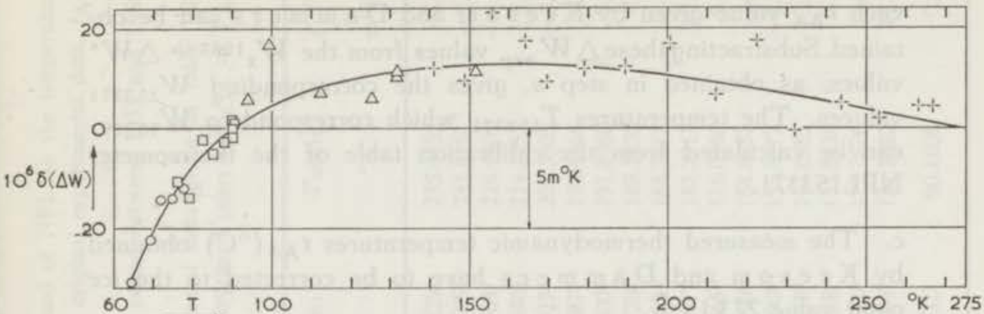

Fig. 6. The deviations of the measured reduced resistance differences $\triangle W_{\text{exp}}$ $(= W_{70} - W_{153371})$ values from a linear relation $\triangle W_{\text{calc}} = -11.42700\ (T - 273.15°\text{K})10^{-6}$. $\delta(\triangle W) = \triangle W_{\text{exp}} - \triangle W_{\text{calc}}$.

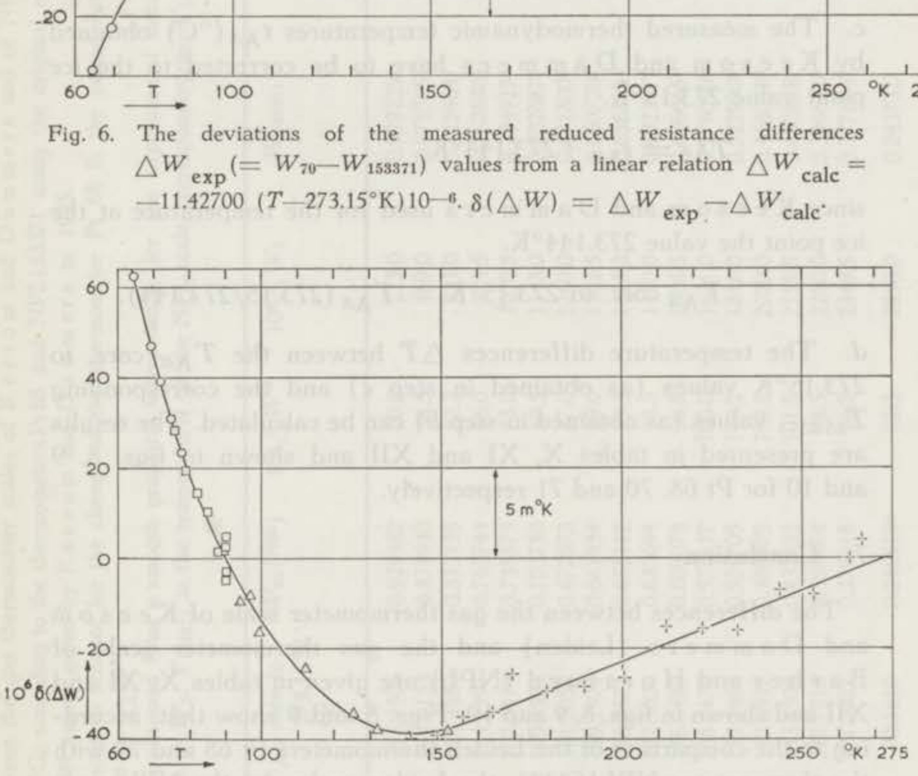

Fig. 7. The deviations of the measured reduced resistance differences $\triangle W_{\text{exp}}$ $(= W_{71} - W_{153371})$ values from a linear relation $\triangle W_{\text{calc}} = -12.54959\ (T - 273.15°\text{K})10^{-6}$. $\delta(\triangle W) = \triangle W_{\text{exp}} - \triangle W_{\text{calc}}$.

to the reduced resistance values $W_x{}^{1935}$ given by Keesom and Dammers, where x refers to the thermometers Pt 68, 70 and 71.
b. Using smooth curves through the measured $\triangle W_{\text{exp}}$ $(= W_x - W_{153371})$ values for each thermometer, according to our measurements (see tables VII, VIII and IX) the $\triangle W_{\text{exp}}$ value at

each $t_{A\alpha}$ value given by Keesom and Dammers can be obtained. Substracting these $\triangle W_{\text{exp}}$ values from the $W_x{}^{1935} + \triangle W^*$ values, as obtained in step *a*, gives the corresponding W_{153371} valuees. The temperatures T_{153371} which correspond to W_{153371} can be calculated from the calibration table of the thermometer NPL153371.

c. The measured thermodynamic temperatures $t_{A\alpha}$ (°C) obtained by Keesom and Dammers have to be corrected to the ice point value 273.15°K.

$$T_{A\alpha} = t_{A\alpha} + 273.144°K$$

since Keesom and Dammers used for the temperature at the ice point the value 273.144°K.

$$T_{A\alpha} \text{ corr. to } 273.15°K = T_{A\alpha}\,(273.15/273.144).$$

d. The temperature differences $\triangle T$ between the $T_{A\alpha}$ corr. to 273.15°K values (as obtained in step *c*) and the corresponding T_{153371} values (as obtained in step *b*) can be calculated. The results are presented in tables X, XI and XII and shown in figs. 8, 9 and 10 for Pt 68, 70 and 71 respectively.

7. Conclusion

The differences between the gas thermometer scale of Keesom and Dammers (Leiden) and the gas thermometer scale of Barber and Horsford (NPL) are given in tables X, XI and XII and shown in figs. 8, 9 and 10. Figs. 8 and 9 show that, according to the comparison of the Leiden thermometers Pt 68 and 70 with the thermometer NPL153371, the Leiden scale and the NPL scale are in close agreement with each other. A maximum deviation of about 12 m°K is found at about –150°C. The average deviation is, according to the comparison of Pt 68 with NPL153371, equal to 4.3 m°C and, according to the comparison of Pt 70 and NPL153371, equal to 0.3 m°C. Figs. 8 and 9 show two maxima and two minima in the deviations. The same small systematic deviations occur also in fig. 10. The average deviation for $T_{\text{Leiden}} - T_{\text{NPL}}$ is, according to the comparison of Pt 71 and NPL153371, equal to 12 m°C. Since

TABLE X

Temperature differences between the gas thermometer scales of Keesom and Dammers and of NPL, in the temperature range between 0 and —183°C, according to the thermometers Pt 68 and NPL153371 using the original experimental data, $t_{A\alpha}$ and the corresponding $W_{68}{}^{1935}$ values given by Keesom and Dammers in 1935.

$\triangle W^{*}$ is a correction introduced to account for the change of the thermometer Pt 68 in the period between 1935 and 1965, therefore, $W_{68}{}^{1965} = W_{68}{}^{1935} + \triangle W^{*}$.

$\triangle W_1 = W_{68}{}^{1965} - W_{153371}$ obtained from a smooth graphical interpolation for the experimental data given in table VII. Then, $W_{153371} = W_{68}{}^{1965} - \triangle W_1$. T_{153371} is the temperature, on the NPL scale, corresponding to W_{153371} and $\triangle T = T_{A\alpha}$ corr. to 273.15°K — T_{153371}.

Date	$t_{A\alpha}$ °C	$T_{A\alpha}$ corr. to 273.15°K °K	W_{68} (1935)	$10^6 \triangle W^{*}$	$10^6 \triangle W_1$	W_{153371}	T_{153371} °K	$\triangle T$ m°K
8.7.1935	— 17.699	255.4506	0.929482	20.0	273.0	0.929229^{0}	255.4452	5.4
	— 30.336	242.8133	0.878940	34.5	469.0	0.878505^{5}	242.8161	—2.8
	— 46.703	226.4460	0.813135	52.7	723.0	0.812464^{7}	226.4504	—4.4
3.5	— 58.919	214.2297	0.763744	66.0	913.5	0.762896^{5}	214.2255	4.2
	— 65.801	207.3479	0.735875	73.0	1020.5	0.734927^{5}	207.3505	—3.0
	— 73.696	199.4524	0.703750	80.5	1143.0	0.702687^{5}	199.4466	5.8
8.7	— 81.243	191.9052	0.672973	87.0	1260.0	0.671800^{0}	191.8960	9.2
3.5	— 83.951	189.1971	0.661934	89.0	1302.5	0.660720^{5}	189.1930	4.1
2.5	— 84.881	188.2671	0.658112	89.3	1317.0	0.656884^{3}	188.2578	10.3
	— 90.846	182.3020	0.633694	93.3	1410.0	0.632377^{3}	182.2913	10.7
	— 97.099	176.0489	0.608078	96.8	1506.5	0.606668^{3}	176.0480	0.9
6.5	—104.500	168.6477	0.577617	100.0	1621.0	0.576096^{0}	168.6457	2.0
	—117.301	155.8464	0.524705	103.2	1818.0	0.522990^{2}	155.8477	—1.3
	—130.452	142.6951	0.469975	103.5	2020.0	0.468058^{5}	142.6985	—3.4
	—139.296	133.8509	0.432882	101.8	2155.5	0.430828^{3}	133.8438	7.1
4.7	—147.365	125.7818	0.398864	98.5	2280.0	0.396682^{5}	125.7676	14.2
	—151.844	121.3027	0.379918	96.2	2349.5	0.377664^{7}	121.2882	14.5
	—182.985	90.1610	0.246519^{4}	62.3	2850.0	0.243731^{7}	90.1608	0.2

TABLE XI

Temperature differences between the gas thermometer scales of Keesom and Dammers and of NPL, in the temperature range between 0 and —183°C, according to thermometers Pt 70 and NPL153371 using the original experimental data, $t_{A\alpha}$ and the corresponding $W_{70}{}^{1935}$ values given by Keesom and Dammers in 1935.
$\triangle W^*$ is a correction introduced to account for the change of the thermometer Pt 70 in the period between 1935 and 1965, therefore, $W_{70}{}^{1965} = W_{70}{}^{1935} + \triangle W^*$.
$\triangle W_1 = W_{70}{}^{1965} - W_{153371}$ obtained from a smooth graphical interpolation for the experimental data given in table VIII. Then, $W_{153371} = W_{70}{}^{1965} - \triangle W_1$. T_{153371} is the temperature, on the NPL scale, corresponding to W_{153371} and $\triangle T = T_{A\alpha}$ corr. to 273.15°K — T_{153371}.

Date	$t_{A\alpha}$ °C	$T_{A\alpha}$ corr. to 273.15°K °K	$W_{70}({}^{1935})$	$10^6 \triangle W^*$	$10^6 \triangle W_1$	W_{153371}	T_{153371} °K	$\triangle T$ m°K
14.6.35	— 26.065	247.0844	0.895982	— 7.6	301.0	0.895673^4	247.0849	— 0.5
	— 42.489	230.6601	0.829989	—12.3	492.0	0.829484^7	230.6598	0.3
	— 54.205	218.9438	0.782718	—15.8	627.0	0.782075^2	218.9494	— 5.6
	— 63.158	209.9906	0.746457	—18.0	731.0	0.745708^0	209.9985	— 7.9
	— 80.863	192.2852	0.674327	—22.0	936.5	0.673368^5	192.2790	6.2
7.6	— 82.900	190.2482	0.666013	—22.7	960.0	0.665030^3	190.2441	4.1
	— 95.598	177.5499	0.613972	—25.0	1103.5	0.612843^5	177.5462	3.7
24.6	—109.099	164.0486	0.558379	—27.1	1257.0	0.557094^9	164.0575	— 8.9
	—122.083	151.0643	0.504479	—28.5	1405.0	0.503045^5	151.0625	1.8
	—134.313	138.8340	0.453453	—29.0	1544.0	0.451880^0	138.8447	—10.7
18.6	—146.765	126.3818	0.400942	—29.0	1685.5	0.399227^5	126.3680	13.8
20.6	—150.366	122.7807	0.385729	—29.0	1726.0	0.383974^0	122.7732	7.5
	—182.983	90.1610	0.245847^3	—24.3	2089.0	0.243734^0	90.1613	— 0.3

TABLE XII

Temperature differences between the gas thermometer scales of Keesom and Dammers and of NPL, in the temperature range between 0 and —183°C, according to the thermometers Pt 71 and NPL153371 using the original experimental data, $t_{\mathrm{A}\varkappa}$ and the corresponding $W_{71}{}^{1935}$ values given by Keesom and Dammers in 1935.

$\triangle W^{*}$ is a correction introduced to account for the change of the thermometer Pt 71 in the period between 1935 and 1965, therefore, $W_{71}{}^{1965} = W_{71}{}^{1935} + \triangle W^{*}$.

$\triangle W_1 = W_{71}{}^{1965} - W_{153371}$ obtained from a smooth graphical interpolation for the experimental data given in table IX. Then, $W_{153371} = W_{71}{}^{1965} - \triangle W_1$. T_{153371} is the temperature, on the NPL scale, corresponding to W_{153371} and $\triangle T = T_{\mathrm{A}\varkappa}$ corr. to 273.15°K — T_{153371}.

Date	$t_{\mathrm{A}\varkappa}$ °C	$T_{\mathrm{A}\varkappa}$ corr. to 273.15°K °K	$W_{71}(^{1935})$	$10^6 \triangle W^{*}$	$10^6 \triangle W_1$	W_{153371}	T_{153371} °K	$\triangle T$ m°K
12.7.35	— 27.507	245.6424	0.890206	—18.0	338.5	0.889849^{5}	245.6361	6.3
	— 39.651	233.4981	0.841436	—19.0	487.5	0.840929^{5}	233.4935	4.6
	— 51.522	221.6269	0.793570	—24.5	633.0	0.792912^{5}	221.6222	4.7
14.6	— 54.206	218.9428	0.782675	—25.9	666.0	0.781983^{1}	218.9267	16.1
3.5	— 58.910	214.2387	0.763687	—27.9	724.0	0.762935^{1}	214.2350	3.7
14.6	— 63.161	209.9876	0.746414	—30.0	776.0	0.745608^{0}	209.9739	13.7
12.7	— 64.928	208.2206	0.739266	—30.5	798.0	0.738437^{5}	208.2124	8.2
3.5	— 65.833	207.3155	0.735576	—31.0	809.0	0.734736^{0}	207.3035	12.0
3.5	— 73.684	199.4644	0.703643	—34.1	904.0	0.702704^{9}	199.4509	13.5
12.7	— 76.603	196.5453	0.691732	—35.3	940.0	0.690756^{7}	196.5276	17.7
3.5	— 83.872	189.2761	0.662035	—38.0	1028.5	0.660968^{5}	189.2535	22.6
12.5	— 90.850	182.2980	0.633492	—40.3	1113.0	0.632338^{7}	182.2819	16.1
	— 97.089	176.0589	0.607890	—42.1	1189.3	0.606658^{6}	176.0458	13.1
11.7	—100.123	173.0248	0.595420	—43.0	1226.0	0.594151^{0}	173.0143	10.5
12.7	—100.265	172.8828	0.594832	—43.0	1228.3	0.593560^{7}	172.8713	11.5
6.5	—104.485	168.6627	0.577412	—44.2	1280.0	0.576087^{8}	168.6437	19.0
	—117.273	155.8754	0.524549	—47.0	1437.0	0.523065^{0}	155.8634	12.0
11.7	—120.458	152.6895	0.511288	—47.3	1475.0	0.509765^{7}	152.6735	15.8
6.5	—130.454	142.6931	0.469640	—48.2	1598.0	0.467993^{8}	142.6831	10.0
	—139.323	133.8239	0.432458	—48.5	1709.5	0.430700^{0}	133.8134	10.5
11.7	—143.610	129.5368	0.414368	—48.3	1764.0	0.412555^{7}	129.5164	20.4
	—153.310	119.8366	0.373324	—48.0	1889.0	0.371387^{0}	119.8141	22.5
	—182.985	90.1610	0.246068^{0}	—39.3	2293.0	0.243735^{7}	90.1617	—0.7

the accuracy of Keesom and Dammers, measurements was estimated to be ± 4 m°C, small differences between the results obtained with the different thermometers may occur, but the deviation of the results obtained with Pt 71 from the average result is somewhat larger.

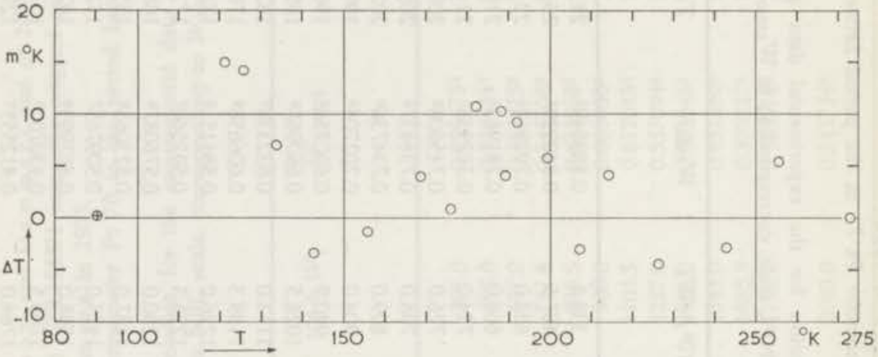

Fig. 8. Temperature differences between the gas thermometer scales of Keesom and Dammers (Leiden) and of Barber and Horsford (NPL), according to the thermometers Pt 68 and NPL153371 using the experimental data given by Keesom and Dammers in 1935 (see table X). $\triangle T = T_{A\varkappa}$ corr. to 273.15°K—T_{153371}.

⊕ The oxygen point.

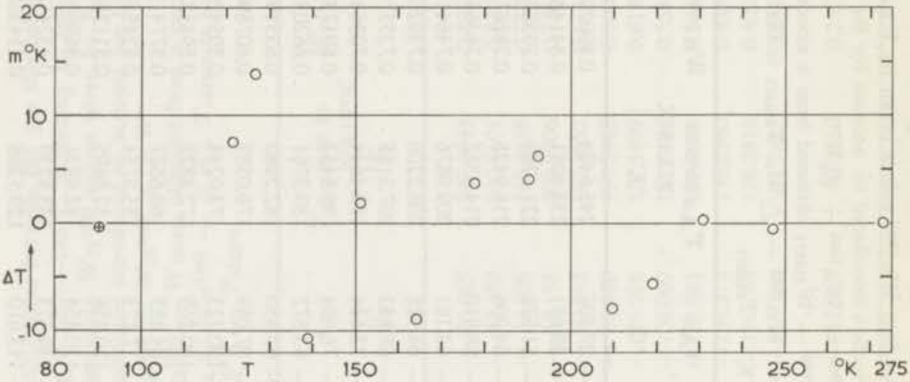

Fig. 9. Temperature differences between the gas thermometer scales of Keesom and Dammers (Leiden) and of Barber and Horsford (NPL), according to the thermometers Pt 70 and NPL153371 using the experimental data given by Keesom and Dammers in 1935 (see table XI). $\triangle T = T_{A\varkappa}$ corr. to 273.15°K — T_{153371}.

⊕ The oxygen point.

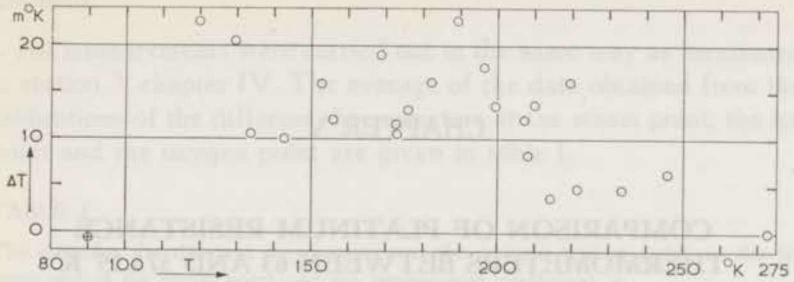

Fig. 10. Temperature differences between the gas thermometer scales of Keesom and Dammers (Leiden) and of Barber and Horsford (NPL), according to the thermometers Pt 71 and NPL153371 using the experimental data given by Keesom and Dammers in 1935 (see table XII). $\triangle T = T_{A\alpha}$ corr. to 273.15°K — T_{153371}.
⊕ The oxygen point.

CHAPTER V

COMPARISON OF PLATINUM RESISTANCE THERMOMETERS BETWEEN 63 AND 373.15°K

1. Introduction

Twelve platinum resistance thermometers were compared with the thermometer NPL153371 in the temperature range from 63 up to 273.15°K, using the apparatus shown in fig. 1, chapter IV. The capsule-type thermometer NPL153371 meets the present requirements of the international Practical Temperature Scale (IPTS) and it was calibrated on the NPL scale at NPL, in the temperature range between 10 and 273.15°K.

The twelve platinum thermometers are made from platinum wire of different origin and of different purity. Their temperature coefficients α range from 0.00391074 to 0.00392642. Three of the thermometers are Pt 68, 70 and 71 made by Dammers at the Kamerlingh Onnes Laboratory in 1935 (see chapter IV). The α coefficients of these three thermometers are between 0.00391074 and 0.00391496. The other nine thermometers are:

1. NPL164956, a capsule-type thermometer made by Tinsley and calibrated on the NPL scale at NPL, Teddington, England.
2. A_2, a capsule-type thermometer kindly put at our disposal by Prof. J. G. Aston, of the Pennsylvania State University, Penn., USA, in 1961.
3. Pt 143, 154 and 157 are capsule-type thermometers made at the Kamerlingh Onnes Laboratory from platinum wire (diameter 0.075 mm, bar 222) obtained from Sigmund Cohn Company, Mount Vernon, New York, USA.
4. Pt 177, 178, 180 and 181 are long-stem thermometers made at the Kamerling Onnes Laboratory from platinum wire of a diameter

of 0.1 mm, provided by Johnson Matthey, Hatton Gardens, London, England.

All measurements were carried out in the same way as mentioned in section 3, chapter IV. The average of the data obtained from the calibrations of the different thermometers at the steam point, the ice point and the oxygen point are given in table I.

TABLE I

The data for the different thermometers at the oxygen boiling point, at the ice point and at the steam point and the temperature coefficient α.

Pt	$W(O_2)$	$R(0°C)$ Ω	$R(100°C)/R(0°C)$	$10^3\alpha$ $°C^{-1}$
NPL153371	0.243815	25.37797	1.392637	3.92637
NPL164956	0.243819	24.27257	1.392636	3.92636
A_2	0.244720	24.31906	1.392085	3.92085
Pt 143	0.243874	23.83076	1.392606	3.92606
Pt 154	0.243805	23.67669	1.392642	3.92642
Pt 157	0.243822	23.37789	1.392632	3.92632
Pt 177	0.244757	18.33145	1.392144	3.92144
Pt 178	0.244705	19.36750	1.392170	3.92170
Pt 180	0.244797	13.39856	1.392116	3.92116
Pt 181	0.249893	17.95350	1.392068	3.92068
Pt 68	0.246664	12.45598	1.391062	3.91062
Pt 70	0.245906	3.42954	1.391484	3.91484
Pt 71	0.246111	12.50621	1.391435	3.91435

Fig. 1 shows the reduced resistance at the boiling point of oxygen, $W(O_2)$, of the thermometers mentioned in table I as a function of the temperature coeifficient α.

2. **Results**

The data of the comparison of the three thermometers of Dammers with the thermometer NPL153371 have been given in chapter IV. Comparisons of the other nine platinum resistance thermometers with the thermometer NPL153371 were carried out in two runs. The measurements of the resistance of the thermometers at each temperature took about 80 minutes. From the measured reduced re-

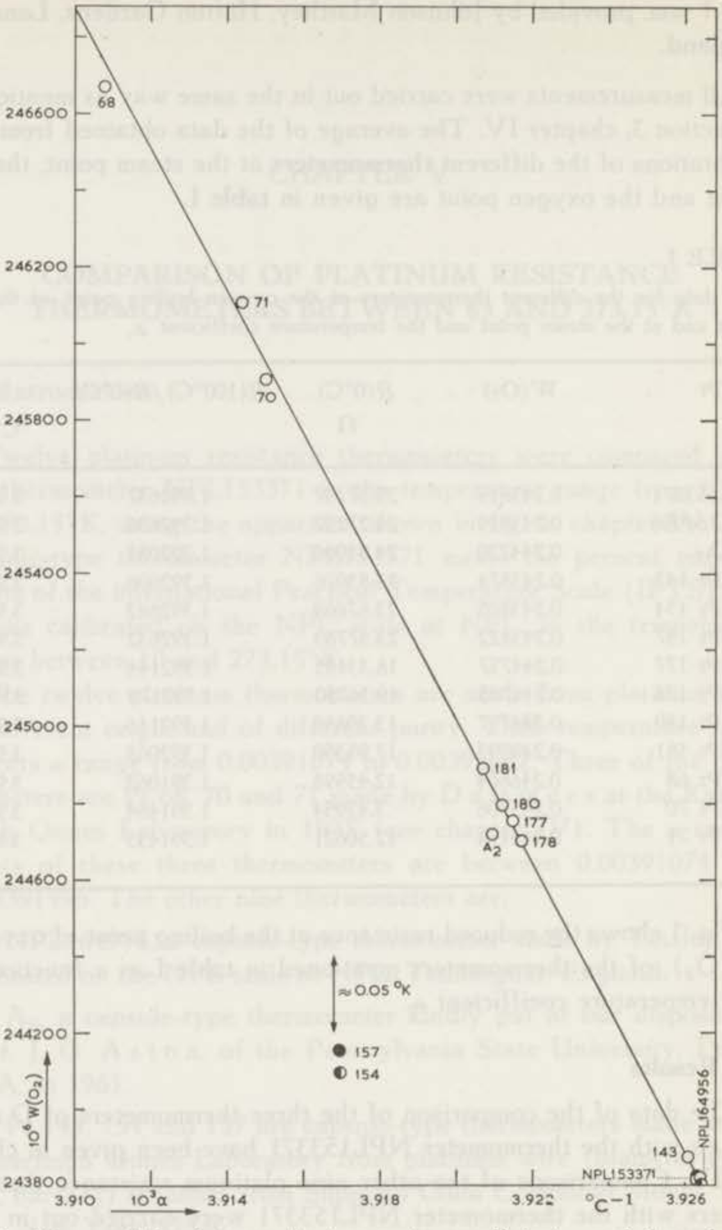

Fig. 1. Linear relation between the temperature coefficient α and the reduced resistance $W(90.18\,^\circ\mathrm{K})$ at the boiling point of oxygen. $W(90.18\,^\circ\mathrm{K}) = 0.978888 - 187.214\,\alpha$.

sistance $W(=R(T)/R(0^\circ\mathrm{C}))$ for the standard thermometer, temperatures T_{153371} on the NPL scale have been derived, using the calibration data provided by NPL in May 1965 for temperatures from 89 up to 273.15°K. For temperatures from 64 up to 90°K the calibration data of the fifteenth September 1961 were used. The temperatures obtained in this way for the range from 64 up to 90°K were decreased by about 3 m°K to obtain a good fit at 90.18°K. The reason for this change is a small change in the calibration of this thermometer at NPL.

Thermometer NPL164956 has been calibrated against the standard thermometer at every series to check its constancy and the reproducibility of the measurements. According to the experimental data (table II) the reproducibility of the measurements is to within ± 1 m°K (see fig. 2).

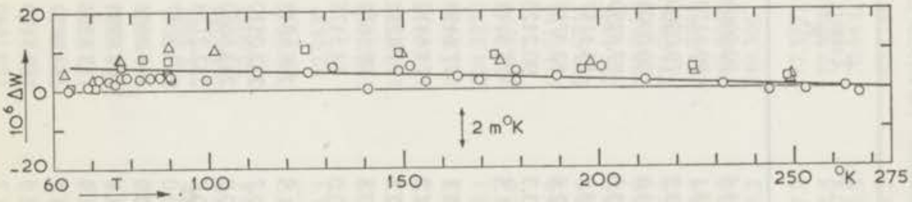

Fig. 2. The measured reduced resistance differences $\triangle W = W_{164956} - W_{153371}$.

○ First run of measurements

□ Second run of measurements

△ Third run of measurements

The experimental data of the nine thermometers are given in tables II to X and the deviation curves $\triangle W = W_x - W_{153371}$ versus T_{153371} are shown in figs. 2 to 4. The subscript x refers to the thermometers NPL164956, A_2, 143, 154, 157, 177, 178, 180 and 181.

3. Conclusion

The results obtained with these thirteen different platinum resistance thermometers which are of different origin and different purity can be summarized as follows:

1. The relation between the difference in reduced resistance $\triangle W$ and the temperature T is, for the five thermometers which are made

TABLE II

Comparison of the thermometer NPL164956 with the thermometer NPL153371.

Date	W_{164956}	W_{153371}	$10^6\triangle W$	T_{153371} °K	Remarks	
					Bath liquid	Series
15. 4.65	0.2434540	0.2434504	3.6	90.0960	O_2	used with the thermometers Pt 68, Pt 70 and Pt 71
	0.2435486	0.2435455	3.1	90.1179		
4. 5	0.1954874	0.1954842	3.2	79.0509		
5. 5	0.2434289	0.2434259	3.0	90.0903		
	0.2327350	0.2327320	3.0	87.6259		
	0.2218304	0.2218273	3.1	85.1157		
	0.2099334	0.2099308	2.6	82.3787		
6. 5	0.2440907	0.2440874	3.3	90.2428		
	0.1819144	0.1819129	1.5	75.9144		
13. 5	0.1894161	0.1894130	3.1	77.6493	N_2	
	0.1764247	0.1764225	2.2	74.6412		
	0.1643394	0.1643366	2.8	71.8282		
14. 5	0.1529713	0.1529705	0.8	69.1670		
	0.1334395	0.1334395	0.0	64.5475		
2. 6	0.9746771	0.9746786	—1.5	266.8042	isopentane	
	0.8351059	0.8351052	0.7	232.0510		
3. 6	0.8819243	0.8819252	—0.9	243.6660		
	0.9202954	0.9202960	—0.6	252.2174		
	0.9602940	0.9602940	0.0	263.2047		
4. 6	0.4612125	0.4612125	0.0	141.0666		
	0.4931835	0.4931789	4.6	148.6998		
	0.5228794	0.5228775	1.9	155.8206		
	0.5571206	0.5571174	3.2	164.0629		
9. 6	0.5798050	0.5798030	2.0	169.5419		
	0.6194720	0.6194703	1.7	179.1549		
	0.6192955	0.6192910	4.5	179.1113		
	0.6614830	0.6614800	3.0	189.3782		
10. 6	0.7550798	0.7550780	1.8	212.3020		
	0.7074111	0.7074059	5.2	200.6019		
30. 6	0.3952418	0.3952375	4.3	125.4267	propane	
	0.2842478	0.2842454	2.4	99.5073		
	0.3399149	0.3399103	4.6	112.4429		
	0.5054484	0.5054427	5.7	151.6370		
	0.4227859	0.4227803	5.6	131.9364		
27. 9	0.1883343	0.1883286	5.7	77.3987	N_2	used with the thermometers Pt 143, Pt 154, Pt 157 and A_2
28. 9	0.1334831	0.1334836	0.5	64.5588		
	0.1604006	0.1603998	0.8	70.9084		
30. 9	0.2423083	0.2423008	7.5	89.8308	O_2	
1.10	0.2125685	0.2125602	8.3	82.9837		
4.10	0.3937118	0.3937005	11.3	125.0643	isopentane	
5.10	0.4953368	0.4953277	9.1	149.2141		
	0.5958058	0.5957970	8.8	173.4130		
	0.6879540	0.6879492	4.8	195.8411		
6.10	0.8038754	0.8038703	5.1	224.3270		
	0.9013598	0.9013572	2.6	248.4994		
19.10	0.3367887	0.3367788	9.9	111.7118	isopentane	used with the thermometers Pt 157 Pt 177 Pt 178 Pt 180 Pt 181
	0.4968385	0.4968294	9.1	149.5737		
20.10	0.6028919	0.6028842	7.7	175.1305		
	0.6970513	0.6970447	6.6	198.0656		
21.10	0.8057535	0.8057470	6.5	224.7906		
	0.8057078	0.8057034	4.4	224.7798		
	0.9046030	0.9045998	3.2	249.3068		
	0.9046017	0.9045995	2.2	249.3067		
25.10	0.1891106	0.1891029	7.7	77.5777	N_2	
	0.1891189	0.1891114	7.5	77.5796		
26.10	0.1601259	0.1601234	2.5	70.8437		
	0.1274641	0.1274599	4.2	63.1188		
2.11	0.2435683	0.2435571	11.2	90.1205	O_2	

TABLE III

Comparison of the thermometer A_2 with the thermometer NPL153371.

Date	W_{A_2}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
27. 9.65	0.1892662	0.1883089	957.3	77.3942	
28. 9	0.1344729	0.1334742	998.7	64.5566	N_2
28. 9	0.1611120	0.1601382	973.8	70.8472	
30. 9	0.2423593	0.2423506	8.7	89.8423	O_2
1.10	0.2135391	0.2126060	933.1	82.9942	
4.10	0.3944426	0.3936864	756.2	125.0610	
5.10	0.4959409	0.4952995	641.4	149.2074	
5.10	0.5963570	0.5958368	520.2	173.4226	isopentane
5.10	0.6883396	0.6879357	403.9	195.8378	
6.10	0.8040331	0.8037751	258.0	224.3035	
6.10	0.9014808	0.9013504	130.4	248.4978	
	1.392085	1.392637	—552.0	373.15	steam point

TABLE IV

Comparison of the thermometer Pt 143 with the thermometer NPL153371.

Date	W_{143}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
28. 9.65	0.1335751	0.1335071	68.0	64.5644	N_2
27. 9	0.1883789	0.1883152	63.7	77.3957	
28. 9	0.1604604	0.1603962	64.2	70.9076	
30. 9	0.2423664	0.2423306	60.4	89.8320	O_2
1.10	0.2126302	0.2125676	62.6	82.9854	
4.10	0.3937334	0.3936818	51.6	125.0599	
5.10	0.4953233	0.4952828	40.5	149.2034	
5.10	0.5958480	0.5958185	29.5	173.4182	isopentane
5.10	0.6879304	0.6879054	25.0	195.8304	
6.10	0.8038693	0.8038540	15.3	224.4230	
6.10	0.9013097	0.9013031	6.6	248.4860	
	1.392606	1.392637	—31.0	373.15	steam point

TABLE V

Comparison of the thermometer Pt 154 with the thermometer NPL153371.

Date	W_{154}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
27. 9.65	0.1883014	0.1883123	—10.9	77.3950	
28. 9	0.1334839	0.1335000	—16.1	64.5627	N_2
28. 9	0.1603661	0.1603766	—10.5	70.9030	
28. 9	0.1601295	0.1601401	—10.6	70.8477	
30. 9	0.2423056	0.2423149	— 9.3	89.8341	
30. 9	0.2423454	0.2423560	—10.6	89.8436	O_2
1.10	0.2125701	0.2125847	—14.6	82.9893	
4.10	0.3936766	0.3936819	— 5.3	125.0599	
5.10	0.4952744	0.4952793	— 4.9	149.2025	
5.10	0.5958150	0.5958205	— 5.5	173.4187	isopentane
5.10	0.6879188	0.6879256	— 6.8	195.8353	
6.10	0.8038315	0.8038320	— 0.5	224.3176	
6.10	0.9013275	0.9013297	— 2.2	248.4926	
	1.392642	1.392637	5.0	373.15	steam point

of very pure platinum wire and have a temperature coefficient α higher than 0.003926, linear between 63 and 373.15°K within the limits of accuracy ($\pm$ 1 m°K) realized in our experiments, see figs. 2 and 3 for NPL164956, NPL153371, Pt 143, 154 and 157. Therefore, for these thermometers $\triangle W$, as a function of T, can be represented simply with

$$\triangle W = a + bT$$

where the constants a and b can be obtained from calibrations at the steam point and the oxygen boiling point.

2. The relation between $\triangle W$ and T is linear within 1 to 2 m°K from 373.15 (steam point) down to about 125°K for the five thermometers which have a temperature coefficient α in the range from 0.00392068 to 0.00392170 (see fig. 4). Below 125°K the $\triangle W$ versus T curve deviates from a straight line and it deviates more rapidly below 90°K. As can be seen from fig. 4, it appears that the shape of the deviation curve depends on the origin or treatment of

TABLE VI

Comparison of the thermometer Pt 157 with the thermometer NPL153371.

Date	W_{157}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
27. 9.65	0.1883184	0.1883093	9.1	77.3943	
28. 9	0.1334814	0.1334715	9.9	64.5559	N_2
28. 9	0.1601381	0.1601299	8.2	70.8453	
30. 9	0.2423593	0.2423506	8.7	89.8423	O_2
1.10	0.2125957	0.2125886	7.1	82.9902	
4.10	0.3936940	0.3936842	9.8	125.0605	
5.10	0.4952854	0.4952779	7.5	149.2022	
5.10	0.5958243	0.5958189	5.4	173.4183	isopentane
5.10	0.6879232	0.6879201	3.1	195.8339	
6.10	0.8038075	0.8038044	3.1	224.3107	
6.10	0.9013425	0.9013411	1.4	248.4890	
19.10	0.3367631	0.3367540	9.1	111.7060	
19.10	0.4968227	0.4968160	6.7	149.5705	
20.10	0.6029033	0.6028950	8.3	175.1331	
20.10	0.6030054	0.6030008	4.6	175.1588	isopentane
20.10	0.6970456	0.6970416	4.0	198.0648	
21.10	0.8056939	0.8056915	2.4	224.7769	
21.10	0.9046074	0.9046075	—0.1	249.3087	
25.10	0.1890934	0.1890857	7.7	77.5737	
25.10	0.1891182	0.1891118	6.4	77.5797	
26.11	0.1601821	0.1601755	6.6	70.8559	N_2
26.11	0.1275191	0.1275133	5.8	63.1316	
	1.392632	1.392637	—5.0	373.15	steam point

the platinum wire. The thermometers A_2 and Pt 177, 178, 180 or 181 deviate in opposite directions specially below 90°K.

For the calibration of such thermometers between 90 and 373.15°K it is advisable to carry out calibrations at more than three fixed points when α is only a little larger than 0.003920. The calibration can be accurate to within 2 m°K if these points are

a. the steam point
b. the ice point
c. a point near the temperature of the sublimation point of CO_2 (*i.e.* 193°K)
d. the oxygen boiling point.

TABLE VII

Comparison of the thermometer Pt 177 with the thermometer NPL153371.

Date	W_{177}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
19.10.65	0.3374732	0.3366488	824.4	111.6814	isopentane
19.10	0.4972603	0.4966326	627.7	149.5265	
20.10	0.6034014	0.6029077	493.7	175.1365	
20.10	0.6974370	0.6970577	379.3	198.0688	
21.10	0.8059759	0.8057256	250.3	224.7853	
21.10	0.9047342	0.9046076	126.6	249.3087	
25.10	0.1901184	0.1891009	1017.5	77.5772	N_2
25.10	0.1901284	0.1891112	1017.2	77.5796	
26.10	0.1611838	0.1601282	1055.6	70.8449	
26.10	0.1286195	0.1275025	1117.0	63.1290	
2.11	0.2444412	0.2434988	942.4	90.1071	O_2
	0.2444616	0.2435200	941.6	90.1119	
	1.392144	1.392637	—493.0	373.15	steam point

TABLE VIII

Comparison of the thermometer Pt 178 with the thermometer NPL153371.

Date	W_{178}	W_{153371}	$10^6 \triangle W$	T_{153371} °K	Bath liquid
19.10.65	0.3374599	0.3366836	776.3	111.6896	isopentane
19.10	0.4972600	0.4966720	588.0	149.5360	
19.10	0.4974118	0.4968226	589.2	149.5720	
20.10	0.6033561	0.6028871	469.0	175.1312	
20.10	0.6034712	0.6029997	471.5	175.1585	
20.10	0.6034597	0.6029928	466.9	175.1568	
20.10	0.6974183	0.6970607	357.6	198.0695	
21.10	0.8059509	0.8057219	229.0	224.7844	
21.10	0.9047266	0.9046119	114.7	249.3089	
25.10	0.1900608	0.1890967	964.1	77.5762	N_2
25.10	0.1900729	0.1891102	962.7	77.5794	
26.10	0.1611393	0.1601401	999.2	70.8477	
26.10	0.1285505	0.1274957	1054.8	63.1274	
26.10	0.1285466	0.1274917	1054.9	63.1264	
2.11	0.2444592	0.2435678	891.4	90.1230	O_2
	1.392170	1.392637	—467.0	373.15	steam point

TABLE IX

Comparison of the thermometer Pt 180 with the thermometer NPL153371.

Date	W_{180}	W_{153371}	$10^6\triangle W$	T_{153371} °K	Bath liquid
19.10.65	0.3375790	0.3367187	860.3	111.6977	
19.10	0.4973943	0.4967426	651.7	149.5529	
19.10	0.4974748	0.4968212	653.6	149.5717	
20.10	0.6033808	0.6028664	514.4	175.1262	isopentane
20.10	0.6974477	0.6970530	394.7	198.0676	
21.10	0.8059676	0.8057144	253.2	224.7825	
21.10	0.9047344	0.9046123	122.1	249.3099	
25.10	0.1901537	0.1890929	1060.8	77.5754	
25.10	0.1901677	0.1891075	1060.2	77.5787	N_2
26.10	0.1612421	0.1601402	1101.9	70.8477	
26.10	0.1286457	0.1274970	1148.7	63.1277	
2.11	0.2445563	0.2435730	983.3	90.1242	O_2
	1.392116	1.392637	—521.0	373.15	steam point

TABLE X

Comparison of the thermometer Pt 181 with the thermometer NPL153371.

Date	W_{181}	W_{153371}	$10^6\triangle W$	T_{153371} °K	Bath liquid
19.10.65	0.3376849	0.3367420	942.9	111.7032	
19.10	0.4975087	0.4967961	712.6	149.5657	
20.10	0.6034339	0.6028635	570.4	175.1255	
20.10	0.6974818	0.6970461	435.7	198.0659	isopentane
21.10	0.8059827	0.8056979	284.8	224.7785	
21.10	0.9047541	0.9046111	143.0	249.3096	
25.10	0.1902506	0.1890907	1159.9	77.5749	
25.10	0.1902690	0.1891089	1160.1	77.5791	
26.10	0.1613580	0.1601547	1203.3	70.8511	N_2
26.10	0.1287642	0.1275021	1262.1	63.1289	
2.11	0.2446573	0.2435795	1077.8	90.1257	O_2
	1.392068	1.392637	—569.0	373.15	steam point

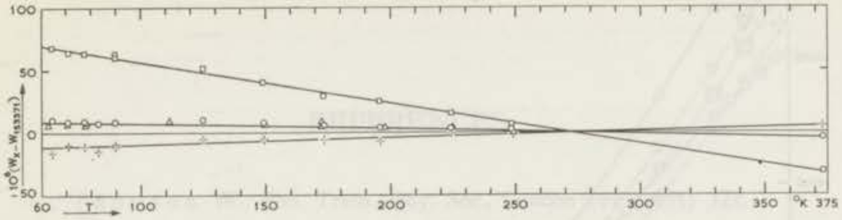

Fig. 3. The measured reduced resistance differences $\triangle W = W_x - W_{153371}$, where x refers to the thermometer Pt 143, 154 or 157.

□ Pt 143
+ Pt 154
△ Pt 157
○ Pt 157

But if these thermometers are to be used also below the oxygen boiling point, e.g. down to 63°K, then, it is advisable to carry out calibrations also below 90°K, e.g. at the boiling point and the triple point of liquid nitrogen. The calibration at the triple point of nitrogen is not difficult, since the pressure at this temperature is still about 94 mm Hg and $dp/dT = 17$ mm Hg/°K.

3. The relation between $\triangle W$ and T is not simple for the three thermometers which have a temperature coefficient α in the range from 0.00391074 to 0.00391496 (see Dammers thermometers, chapter IV), especially at lower temperature, e.g. < 140°K. $\triangle W$ deviates more and more rapidly from a linear relation in T, (see figs. 5 to 7 in chapter IV). For the calibration of such thermometers between 90 and 373.15°K, it seems desirable that more than four fixed points be used to reach an accuracy to within 2 m°K.

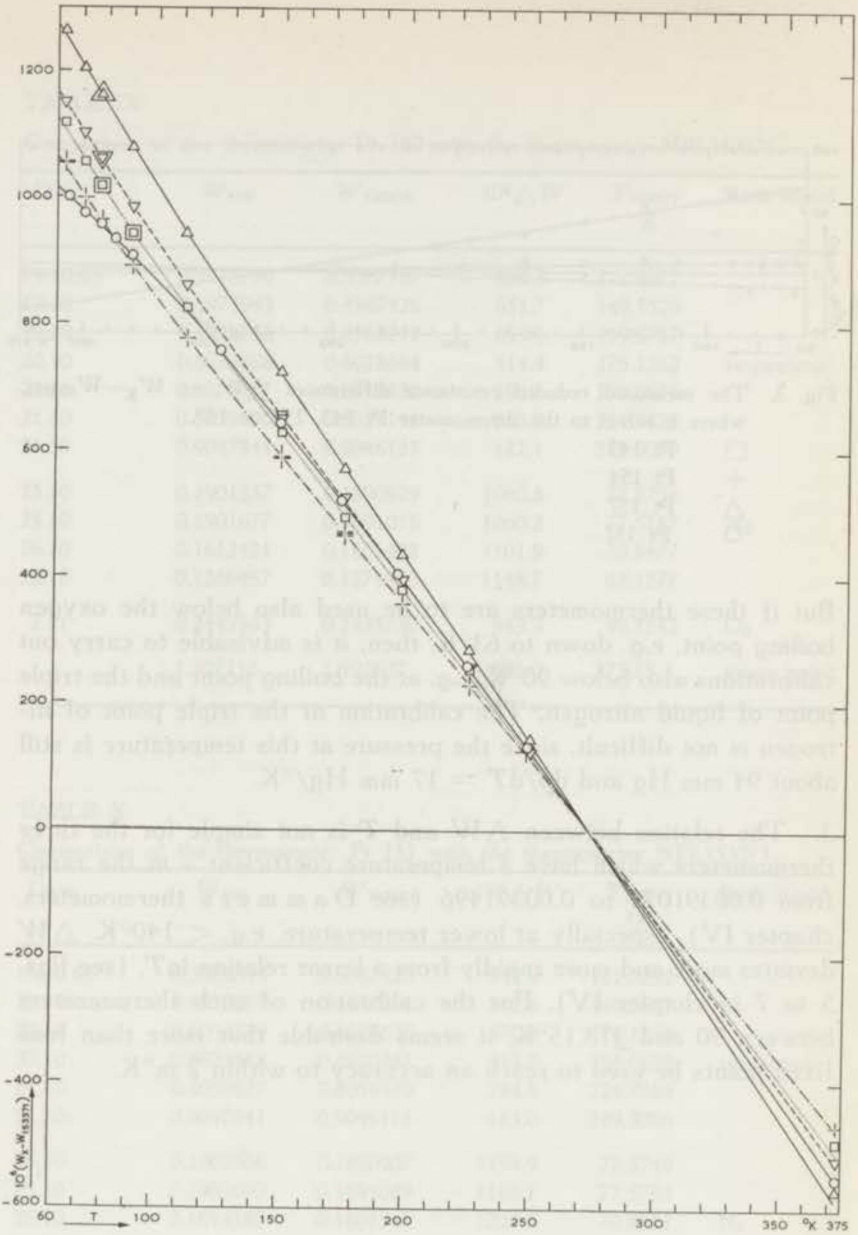

Fig. 4. The measured reduced resistance differences $\triangle W = W_x - W_{153371}$, where x refers to the thermometer A_2, Pt 177, 178, 180 or 181.

○ A_2
□ Pt 177
-¦- Pt 178
▽ Pt 180
△ Pt 181

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SUMMARY

This thesis deals with:

1. *The study of the vapour pressure-temperature relation of liquid nitrogen.*

The vapour pressure-temperature relation of liquid nitrogen can be obtained from direct measurements of p and T and from thermodynamic calculations. In chapter II we used a thermodynamic equation (eq. (1)) to calculate the temperature dependence of the pressure of the saturated vapour of liquid nitrogen. The calculated p-T relation is given in table II, chapter II. The accuracy of this calculated p-T relation is limited by the uncertainties in the data for the thermodynamic quantities which were used in the calculations. The p-T relation was also determined directly from simultaneous measurements of the vapour pressure and of the resistances of five platinum thermometers which had been calibrated either on the gas thermometer scale of the National Bureau of Standards (USA), or of the National Physical Laboratory (England) or of the Physico-technical and Radio-technical Measurements Institute (USSR). Temperatures T_{p} derived from the pressure measurements using table II, chapter II, were compared with temperatures $T_{\mathrm{CCT\text{-}64}}$, on the CCT-64 scale, derived from the thermometer readings. The CCT-64 temperature scale can be considered as an average of four existing temperature scales. It has been recommended by the Comité Consultatif de Thermométrie in 1964 as a provisional scale. The results are shown in figs. 7 to 11 in chapter III. In these figures a smooth curve was drawn. This curve represents a smooth average of $T_{\mathrm{CCT\text{-}64}} - T_{\mathrm{p}}$ according to table XI of chapter III, and table II of chapter II. According to this smooth curve the maximum difference between $T_{\mathrm{CCT\text{-}64}}$ and T_{p} is nowhere more than 1.3 m°K between 63 and 77.5°K, while above 77.5°K the deviation increases gradually up to 7 m°K at 85°K.

Table XI, chapter III, is a very good representation of our experimental data. It gives the pressure of the saturated vapour of liquid nitrogen as a smooth function of $T_{\text{CCT-64}}$, according to equation (10), chapter III, and enables the determination of temperatures on the CCT-64 scale between 63 and 85°K from accurately measured vapour pressures with a high precision and without the use of platinum thermometers. The CCT-64 scale is a good realization of the thermodynamic temperature scale between 63 and 85°K.

We found for the boiling point and the triple point temperatures of liquid nitrogen the values 77.3385 and 63.1420°K respectively on the CCT-64 scale (see section 8, chapter III) and for the triple point pressure the value 93.921 mm Hg at 0°C and standard gravity (980.665 cm/s^2).

2. *The measurement of temperature differences between the gas thermometer scales of Leiden and of NPL in the temperature range from 0 down to −183°C.*

Chapter IV deals with a direct comparison between the gas thermometer scales of Keesom and Dammers (Leiden), and of Barber and Horsford (NPL). Five platinum thermometers were used, three of these five thermometers were calibrated by Keesom and Dammers, in 1935, against a helium gas thermometer between 0 and −153°C and at −182.983°C and the other two thermometers were calibrated by Barber in 1965 at NPL on the NPL scale between 0 and −183°C. According to our results, the agreement between the Leiden andNPL gas thermometer scales is within 10 to 15 m°K.

3. *Comparison of platinum resistance thermometers between 63 and 373°K.*

A comparison of 13 platinum resistance thermometers from different origin and quality has been carried out in the temperature range between 63 and 373.15°K (see chapter V). The temperature coefficients of these 13 thermometers range from 0.00391074 to 0.00392642°C^{-1}.

SAMENVATTING

In dit proefschrift worden drie onderzoekingen besproken.

1. *De dampspanning van vloeibare stikstof als functie van de temperatuur, in het temperatuurgebied tussen 63 en 85°K.*

De relatie tussen de dampspanning van vloeibare stikstof en de temperatuur (p-T relatie) kan verkregen worden door rechtstreekse metingen van de dampspanning en de temperatuur, en door thermodynamische berekeningen waarbij men uitgaat van gemeten en berekende thermische en calorische grootheden van gasvormige en vloeibare stikstof. Bij de berekeningen wordt in dit proefschrift verondersteld dat de p-T relatie bij tenminste één temperatuur bekend is.

Bij de rechtstreekse metingen van p en T is gebruik gemaakt van platina-weerstandsthermometers die gecalibreerd zijn in een gasthermometerschaal. Deze ijkingen geschiedden in het National Bureau of Standards in Washington, het Instituut voor Physisch-technische en Radio-technische metingen in Moskou, en het National Physical Laboratory in Teddington (Engeland). De gasthermometer-temperatuurschalen van deze drie Instituten verschillen onderling enkele honderdsten van een graad en daarom zijn alle gemeten temperaturen herleid tot temperaturen op de CCT-64-temperatuur-schaal. Deze laatste schaal is in 1964 ter nadere bestudering aanbevolen door het Comité Consultatif de Thermométrie, één van de adviserende commissies van het Comité International van het Bureau International des Poids et Mesures in Sèvres (Frankrijk).

Voor de thermodynamische berekening is een keuze gemaakt uit de vele ter beschikking staande gegevens. Als eindresultaat is een p-T relatie gegeven die p geeft als functie van $T_{\mathrm{CCT\text{-}64}}$ volgens de rechtstreekse metingen en die in goede overeenstemming is met de thermodynamische berekeningen.

2. *Vergelijking van de gasthermometer-metingen van Keesom en Dammers (Kamerlingh Onnes Laboratorium) met de gasthermometer-temperatuurschaal van het National Physical Laboratory in Teddington, in het temperatuurgebied tussen 0 en —183°C.*

Een rechtstreekse vergelijking is uitgevoerd van thermometers die in 1935 door Keesom en Dammers tegen een gasthermometer gecalibreerd zijn, met thermometers die in het National Physical Laboratory in Teddington gecalibreerd zijn. Het blijkt dat de twee gasthermometerschalen met elkaar overeenstemmen binnen 15 m°K.

3. *Vergelijking van platina-weerstandsthermometers tussen 63 en 373°K.*

Dertien platina-weerstandsthermometers die gemaakt zijn van platinadraad van verschillende zuiverheid en verschillende herkomst zijn met elkaar vergeleken tussen 63 en 373°K.

STELLINGEN

I

Zolang er geen platinadraad beschikbaar is van een aanzienlijk hogere zuiverheid dan het draad waar tegenwoordig platina-weerstandsthermometers van worden gemaakt, en zolang er geen nadere gegevens beschikbaar zijn over de weerstand van platinadraden van verschillende zuiverheid, zou het nuttig zijn als het Internationale Bureau voor Maten en Gewichten in Sèvres platinadraad van een hoge kwaliteit en vaste samenstelling beschikbaar zou kunnen stellen voor de constructie van platina-weerstandsthermometers.

II

De dampspanningen van vloeibare zuurstof en stikstof kunnen worden gebruikt om temperaturen te meten, als de relaties tussen deze dampspanningen en de temperatuur bekend zijn. Voor nauwkeurige thermodynamische berekeningen van deze relaties, is het gewenst nieuwe metingen te verrichten van de viriaalcoëfficiënten van zuurstof- en stikstofgas.

III

De gegevens van Keesom en Dammers en die van Barber en Horsford betreffende de vergelijking van de Internationale praktische temperatuurschaal met de thermodynamische temperatuurschaal in het temperatuurgebied tussen −183°C en 0°C, zijn goed met elkaar in overeenstemming. Uit de vergelijking van de genoemde gegevens volgt, dat deze resultaten kunnen worden gebruikt voor de vaststelling van een meer nauwkeurige Internationale praktische temperatuurschaal.

Dit proefschrift, Hoofdstuk IV.

IV

De conclusie van Mittleman, dat de verhouding van de werkzame doorsneden voor enkelvoudige en dubbele ionisatie van He atomen door elektronen, bij een voldoend hoge energie van de elektronen onafhankelijk van deze energie is, is onjuist.

Mittleman, M. H., Phys. Rev. Letters **16** (1966) 498.

V

Jaklevic e.a. beschrijven hun experimenten over het gedrag van twee supergeleiders die met elkaar verbonden zijn door twee parallelle zogenaamde zwakke contacten, op een zodanige wijze, dat het onmogelijk is om hun conclusie, dat de gemeten effecten het gevolg zijn van interferentieverschijnselen, te verifiëren.

Jaklevic, R. C., Lambe, J., Mercereau, J. E. and Silver, A. H., Phys. Rev. **140** (1965) A1628.

VI

Het is van belang de soortelijke warmte en susceptibiliteit van $CuK_2Pb(NO_2)_6$ bij lage temperaturen te onderzoeken.

VII

Het is gewenst de mogelijkheid te onderzoeken om spanningsvrij koperdraad te gebruiken voor de constructie van wederkerigeinductiespoelen, die voor magnetische temperatuurmetingen bij lage temperaturen worden gebruikt.

VIII

Ghozlan maakt de opmerking: „It is generally believed by non-Moslems that a Moslem man could marry more than one wife. This is not correct". Deze opmerking is volgens de Koran onjuist.

Ghozlan, A. I., Academisch proefschrift, Leiden (1963).

IX

De regel dat het van rechts komende verkeer voorrang heeft is te gevaarlijk bij het moderne verkeer.

X

De niet-religieuze culturele verbanden worden in deze tijd voor vele mensen in verschillende opzichten sterker dan de religieuze verbanden.

Stellingen behorende bij het
proefschrift van M. R. M. Moussa