VAPOUR PRESSURES OF OXYGEN AND PLATINUM THERMOMETRY BELOW 100 K

R. MUIJLWIJK

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AAN MIJN MOEDER

AAN MARIANNE

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CHAPTER I

INTRODUCTION

1. Methods of temperature measurement between 10 K* and 100 K.

The methods to measure temperatures between 10 K and 100 K may be divided in two categories:

a. Methods in which instruments are used for which the relation between the measured quantity and the thermodynamic temperature can be derived from theory (the primary thermometers).

b. Methods in which instruments are used for which the relation between the measured quantity and the temperature must be determined experimentally (the secondary thermometers).

The instruments that can be used between 10 K and 100 K belonging to the first group are: the gas thermometer, the acoustic thermometer, the magnetic thermometer and the vapour pressure thermometer. The most widely used instruments belonging to the second group are: the platinum resistance thermometer, thermocouples of copper versus constantan or of other combinations of metals, the germanium resistance thermometer and the carbon resistance thermometer.

The distinction between the two groups is in practice not always very sharp, because for the use of all instruments of the first group some pre-information concerning the properties of the instrument must be known before accurate temperature measurements are possible.

For a constant volume gas thermometer for example one needs a reasonably accurate knowledge of the change of the volume of the

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* The symbol K for kelvin, the unit of temperature, is used instead of °K according to a recent recommendation of the Comité Consultatif des Unités and the Comité Consultatif de Thermométrie of the Bureau International des Poids et Mesures. It was recommended not to change the symbol °C because C is already in use for the coulomb, the unit of electric charge.

reservoir with temperature and even if the pressure of the gas in the reservoir is rather low the deviations from the ideal gas state are too large to obtain accurate results without information on the virial coefficients of the gas.

Non-ideal gas is also used in the acoustic thermometer.

The use of the magnetic thermometer requires the knowledge of at least two or three calibration temperatures. The magnetic thermometer is expecially valuable at very low temperatures because the measured quantity is in first approximation proportional to the inverse of the thermodynamic temperature.

The vapour pressure thermometer was originally used as a secondary thermometer. It was calibrated directly or indirectly against a gas thermometer and the relation between the pressure (p) of the saturated vapour above the condensed gas and the temperature (T) was represented by more or less arbitrary functions. But gradually the thermodynamic p,T relation became more in use and the thermometer came closer to the qualifications of a primary thermometer. To calculate the thermodynamic p,T relation accurately, information on several properties of the gaseous and condensed phases, one or two calibration temperatures and a provisional p,T relation are required. This information was obtained experimentally for several gases used in the low temperature range. For ^{4}He, ^{3}He and H_2 the p,T relations are known today fairly accurately. Recently also p,T relations for nitrogen and oxygen have been deduced on a thermodynamic basis. The vapour pressure thermometer can be very useful in the temperature range where the pressure is not too low for accurate measurements and not inconveniently high. In the proper temperature range the vapour pressure thermometer has the advantage over secondary thermometers that the interpolation between calibration temperatures, that are determined with a gas thermometer, is possible with a well-defined function which is based on thermodynamics instead of with a more or less arbitrary formula. Another advantage of a vapour pressure thermometer is that any sample of the gas, if sufficiently purified, may be used directly for temperature measurements. The vapour pressure thermometer can be smaller than a gas thermometer. It can have a rather low heat capacity and can be quick responding. In its proper temperature range it is more sensitive and reproducible than a gas thermometer.

The main advantages of the best secondary thermometers over a

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gas thermometer for practical temperature measurements are: the convenience of easier thermometer readings, the higher sensitivity and better reproducibility and the smaller size and smaller heat capacity which makes it possible to reach rapidly equilibrium between the secondary thermometer and its surroundings. The main disadvantage of secondary thermometers is the need of extensive calibration, because the relation between the measured quantity and the temperature is not accurately known from theory and because the properties of different thermometers of the same type can differ considerably.

Among the secondary thermometers the platinum resistance thermometer is the most important one in the temperature range under consideration. The difficulties in relating with sufficient accuracy the resistance ratio $W(T)$ $(=R(T)/R(0^{\circ}C))$ of a thermometer to the thermodynamic temperature or to the resistance ratio of another thermometer are now mainly surmounted by the use of very pure platinum and proper formulae for $W(T)$ and $\triangle W(T)$, the difference in $W(T)$ of two thermometers, which are based on accurate calibrations against a gas thermometer and on theoretical considerations. The use of pure platinum and of these formulae has reduced considerably the number of calibrations required for adequate temperature measurement.

A good aid to check the reproducibility of all thermometers and to make the calibration of secondary thermometers easy is found in the use of fixed points. In general these are reproducible temperatures realized as equilibrium states of two phases of a pure substance under standard conditions or triple points. The most important fixed points in the temperature range between 10 K and 100 K are the normal boiling points and the triple points of hydrogen, nitrogen and oxygen. Also the boiling points of neon, argon and carbon monoxyde and the triple points of neon, argon, carbon monoxyde, methane and propane and the transition points in solid nitrogen, oxygen and carbon monoxyde are in this temperature range, but, because of the use of hydrogen, nitrogen and oxygen as cooling liquids, the fixed points that are first mentioned are easier to realize and consequently better known.

The reproducibility of platinum resistance thermometers is an order of magnitude better than the agreement between gas thermometer measurements of different authors. This is one of the reasons why practical temperature scales, which are not identical

with the thermodynamic scale, are used. Another reason is that the definition of a practical scale provides a convenient system for the calibration of thermometers. The definition of a practical scale is intended to be such that, for most practical purposes, the deviations from the thermodynamic scale may be neglected.

An example of a practical scale which can be used in a limited temperature range is the T_{58} scale. This scale consists of a table of T values and corresponding values of the vapour pressure of liquid helium. With the helium vapour pressure thermometer very reproducible results can be obtained and the table was made in such a way that the agreement with the thermodynamic scale was the best that could be obtained in 1958.

2. Developments in platinum thermometry between 10 K and 100 K after 1900.

A resistance thermometer of which the resistance coil is made from strainfree wound wire of very pure platinum has been known for a long time already as a convenient instrument that can be used for temperature measurements with high precision. It has a high reproducibility even many years after it is calibrated. A historical survey of the research on the calibration of platinum thermometers below 100 K shows the gradual progress to a generally acceptable practical temperature scale for the temperature range between 10 K and 100 K.

In 1902 Meilink [1] compared in Leiden a platinum thermometer with the hydrogen gas thermometer at 8 temperatures between 0°C and 63 K. Three calibration temperatures were below 100 K.

Kamerlingh Onnes and Clay [2] compared in 1905 and 1906 the platinum thermometer Pt I with the hydrogen gas thermometer at 2 temperatures in the liquid hydrogen range, at 5 temperatures in the liquid oxygen range and at 6 temperatures between 100 K and 0°C.

In 1907 and 1908 calibrations at low temperatures of the thermometer Pt' I (the same wire as Pt I but wound anew) were carried out by Kamerlingh Onnes and Clay [3] and by Kamerlingh Onnes and Braak [4].

At the Physikalisch Technische Reichsanstalt in Berlin Henning [5] compared in 1912 four thermometers with the hydrogen gas thermometer at 80 K and 90 K and between 120 K and 0°C. From the results he computed a table for the thermometer Pt 32 in which the resistance ratio W is given at integral values of the

temperature between 80 K and 280 K and he discussed a method to relate the W values of different thermometers to each other in this temperature range.

Kamerlingh Onnes and Holst [6] compared in 1913 the thermometer Pt'I again with the hydrogen gas thermometer and with the helium gas thermometer and, using all information about the thermometer Pt'I, Holst [7] computed an interpolation table in which W is given at intervals of one kelvin between 56 K and 91 K and at intervals of five kelvins between 90 K and 0°C. Holst compared the results of Henning with the table for Pt'I using Hennings interpolation formula for differences in W values.

A table in which W values of a certain standard thermometer are given at small intervals of temperature in fact establishes a temperature scale which can be reproduced by calibration of other thermometers against the standard thermometer.

In 1917 Cath, Kamerlingh Onnes and Burgers [8] published results of comparisons of the thermometers Pt 21 and Pt 26 with the helium gas thermometer at 30 temperatures between 14 K and 100 K and at 9 temperatures between 100 K and 0°C. Fifteen of these comparisons were carried out between 21 K and 56 K.

In 1926 the results of the calibration of the thermometer Pt 29 against a gas thermometer by Henning at the P.T.R. were collected in a table of W values at integral values of the temperature between -257°C and -252°C and between -200°C and 0°C [9].

In Leiden Tuyn [10] did the same in 1926 for the thermometers Pt 23 and Pt 23' on the basis of experimental information obtained about ten years earlier. The table of Pt 23' covers the whole temperature range from -270°C to -80°C.

Henning and Otto gave in 1932 the results of the calibration of four platinum thermometers against a gas thermometer between 14 K and 80 K to complete the scale for low temperatures of the P.T.R. [11].

In 1938 the results of the comparison of four platinum thermometers with a helium gas thermometer between -258°C and -190°C were given by Keesom and Bijl [12]. This research was an extension of the measurements of Keesom and Dammers between -183°C and 0°C.

In 1939 Hoge and Brickwedde at the National Bureau of Standards in Washington compared two platinum resistance thermometers and a platinum-10%rhodium resistance thermometer with a helium gas thermometer at many temperatures below the boiling point of

oxygen and compared one of the platinum thermometers with four other platinum thermometers [13]. The primary fixed point for these measurements was the normal boiling point of oxygen. According to results obtained at the P.T.R., 90.19 K was taken for the temperature of this point. A table was deduced from the results for the thermometer L6 in which smoothed values for the resistance ratio of the thermometer were given at small intervals of temperature between 10 K and 92 K. This temperature scale is reproduced in many other thermometers and is still maintained at the N.B.S. The scale is called the NBS-1939 scale. In 1955 the scale of Hoge and Brickwedde was lowered over the whole range by 0.01 K to obtain a better agreement between the scale and the best values known in 1955 for the boiling points of hydrogen and oxygen. The revised scale is called the NBS-1955 scale.

At the Pennsylvania State University eight platinum thermometers were calibrated against a helium gas thermometer by Moessen, Aston and Ascah [14] in 1952. These authors made an independent determination of the boiling point of oxygen starting at the ice-point [15] and measured also the temperature at the boiling point of normal hydrogen. They did not give a smoothed representation of their measured W and T values, but the results could be used as a scale on which other thermometers were calibrated. This scale is called the PSU scale.

The establishment of the scale of the Physical and Radiotechnical Measurements Institute in Moscow (the PRMI scale), based on four platinum thermometers, was published in 1954 by Borovik-Romanov, Orlova and Strelkov [16]. Information concerning this scale is also given in ref. 17 and ref. 18. In 1960 this scale was changed due to the recalculation of the expansion of the copper gas thermometer bulb used in the measurements in 1954 [19].

The last scale established in the same way is the scale of the National Physical Laboratory in Teddington (G.B.) [20, 21]. This NPL scale is based on measurements of Barber in 1960. He also measured the temperatures of the normal boiling points of oxygen and 20.4 K-equilibrium hydrogen.

All these scales are convenient for the measurement of low temperatures. However, the use of many different scales of this type also has a few disadvantages. These scales can only be reproduced as long as there are calibrated thermometers which are in good condition. This disadvantage can be eliminated partly by

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the determination of fixed points on the scale. Difficulties can arise in relating the results of different authors to each other when many slightly different temperature scales are in use, and if the developments in thermometry proceed in this way the number of scales will still increase. For, institutes which do not have their own scales are too strongly dependent on other institutes for temperature measurements with high precision.

In 1961 at an unofficial meeting of members of the Comité Consultatif de Thermométrie at the Bureau International des Poids et Mesures (C.C.T.) preceeding the third symposium on thermometry held in Columbus, Ohio, the possibilities were discussed to compare temperature scales below 90 K. A Working Group of the C.C.T., which was formed in 1962 to study in particular the improvement of the International Practical Temperature Scale below 0°C and the extension of the IPTS below 90 K, agreed that, although the quality of the thermometers used by Keesom and Bijl was of the same order as the quality of the original thermometers of Hoge and Brickwedde, the scale of Keesom and Bijl should not be compared with the other four most recent scales because no capsule-type thermometers were calibrated in this scale and the size of the original thermometers was rather big. Each of the four laboratories whose scales had to be compared would provide two calibrated capsule-type platinum thermometers with resistances at the ice point of about 25 Ω to be compared with each other at the N.P.L. and later on at the P.R.M.I. The results of the comparisons were presented to the C.C.T. in 1964 [22,23,24] and were published in Metrologia in 1966 [25].

Using the results of the comparison of the scales, four tables were calculated at the P.R.M.I. in which the "smoothed average reduced temperature" was given at small steps of the weighted average of the W values of the thermometers [24]. One of these tables, the table B1, was recommended for provisional use as an interpolation table at the meeting of the C.C.T. in 1964. The table was extended by Barber and Hayes [26] to 273.15 K using recent data obtained for temperatures between 90 K and 273.15 K by Barber and Horsford [27]. The complete table was issued by the P.R.M.I. as "Table moyenne normale CCT-64 pour le domaine de 12 à 273.15 K".

The table and the comparison data may be used to define a temperature scale. This fact was realized by the C.C.T. in 1964,

and from the data of the scale comparisons at the N.P.L. and the P.R.M.I. we have calculated in 1965 the differences between this CCT-64 scale and the four national scales (see ref. 28 and section III-3). Details of the CCT-64 scale are given in section III-1. This CCT-64 scale, however, is once more a scale based on calibrated platinum resistance thermometers with the disadvantages mentioned above.

The C.C.T. stated some years ago that the next step in practical temperature measurement in the temperature range under consideration should be the definition of a scale that can be reproduced in every laboratory where a suitable equipment is available. Such a scale may be based on fixed point calibrations of platinum thermometers in conjunction with rules to interpolate the differences in W values between individual thermometers and a standard table between fixed points. The agreement between this scale and the thermodynamic scale must be so good that the differences are negligible for nearly every practical purpose.

Lovejoy at the National Research Council in Ottawa prepared in 1965 a concrete proposal for a temperature scale [29] based on the CCT-64 table and fixed point calibrations. Unfortunately he called this scale also "CCT-64 scale". A distinction between the two scales was made by adding to the name CCT-64 the initials of the authors. So the scale of which we calculated the differences with the national scales is the CCT-64(MDD) scale and the scale proposed by Lovejoy is the CCT-64(L) scale. For the representation of the results of the research described in this thesis only the CCT-64(MDD) scale is used.

Lovejoy revised his proposal a little in 1966 [30] and on the basis of this revised proposal an extension and a revision of the definition of the International Practical Temperature Scale (IPTS) was prepared in 1967 by Barber in cooperation with Van Dijk and Durieux, as agreed on the meeting of the Working Groups of the C.C.T. in Moscow in 1966 [31]. In 1966 the aim of the C.C.T. was to come to an agreement about this text in 1967 so that still in that year the new IPTS could be adopted. In the meantime some opposition arose against the scale, but in September 1967 agreement about the principles of the new IPTS was reached by the C.C.T. at a meeting at the N.R.C. in Ottawa. It was decided that a final draft will be prepared by Barber, Durieux and Preston-Thomas. It has to be ready in November 1968.

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This draft for the new scale will be submitted to The Comité International des Poids et Mesures. This committee got in November 1967 the consent of the Conférence Générale of the B.I.P.M. to adopt the new scale as the official definition of the International Practical Temperature. It is expected that the new IPTS will be promulgated at the beginning of 1969.

To distinguish the new scale from the old IPTS of 1948 we will call it "IPTS-1968" and temperatures on this scale will be denoted T_{68}. Details of the recommendations for the IPTS-1968 are given in section III-2.

3. Summary of this research.

The accurate determination of p, T relations of cryogenic liquids is an important part of the research program of the thermometry section of the Kamerlingh Onnes Laboratory in the last twenty years. Also part of the program of research are investigations on the behaviour of platinum thermometers at low temperatures and on the extension of the IPTS below the boiling point of oxygen.

This thesis deals with the p, T relation of liquid oxygen, the comparison of the p, T relations of hydrogen and oxygen with i.a. the CCT-64 scale, the comparison of methods for the calibration of platinum thermometers below 90 K, and with the reproducibility of platinum thermometers at liquid helium temperatures. Special attention is paid to the measurements at the normal boiling points of 20.4 K-equilibrium hydrogen (e-hydrogen or $e-H_2$) and oxygen, the triple points of e-hydrogen and oxygen and at the transition points at 24 K and 44 K in solid oxygen. The results obtained also provided a possibility to observe the behaviour of platinum resistance thermometers between liquid helium and liquid hydrogen temperatures.

The sequence in which the different subjects are presented is as follows.

In chapter II a thermodynamic equation is given from which the p, T relation of oxygen can be calculated and a choice is made from the available experimental data for all thermodynamic quantities involved in the calculation. The p, T relation resulting from the thermodynamic calculation is compared with p, T data obtained experimentally by other authors.

In chapter III details of the CCT-64 scale and the proposed

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IPTS-1968 are given together with the differences between the principal temperature scales for temperatures below the boiling point of oxygen.

In chapter IV the three slightly different methods of measurements at thermal equilibrium of the resistances of a number of platinum thermometers and the pressures in a vapour pressure thermometer containing helium or e-hydrogen or oxygen that are used in this research are described and the direct results of the measurements are presented.

Chapter V deals with the comparison of the temperatures obtained from the measured resistances of the platinum thermometers with the temperatures obtained from the vapour pressure measurements, and with the results of the measurements at the fixed points.

In chapter VI several methods for the calibration of platinum thermometers between 13.8 K and 90.2 K are compared, and the use of platinum thermometers between 4.2 K and 14 K is discussed.

CHAPTER II

THE VAPOUR PRESSURE– TEMPERATURE RELATION
OF LIQUID OXYGEN

1. The thermodynamic p, T relation.

A thermodynamic equation which gives the relation between the pressure of the saturated vapour above a liquid and the thermodynamic temperature has been derived by Van Dijk [32]. The derivation starts with the conditions for the equilibrium of two phases of one component. The condition $G_G = G_L$ is equivalent with $H_G - H_L = T(S_G - S_L)$ where G is the Gibbs function, H the heat function and S the entropy. The subscripts G and L refer to the gas and liquid phases respectively. $H_G - H_L$ and $T(S_G - S_L)$ are both expressions for the heat of vaporization L. These expressions can be rewritten using the heat of vaporization at the normal boiling point and the temperature at the normal boiling point as reference data and using the equation of state of the gas. When the two expressions for L are equated the following expression for the p, T relation is obtained:

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

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

where: C_{Vi} is the molar heat capacity at constant volume of the gas in the ideal gas state,

C_L is the molar heat capacity of the liquid at saturation pressure,

V_L is the molar volume of the liquid at saturation pressure,

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$(dp/dT)_s$ is the derivative of the pressure of the saturated vapour considered as a function of T,

η and ϵ are corrections due to the non-ideality of the gas and the index 1 refers to the value of the quantity at the normal boiling point.

For the equation of state of oxygen gas is used: $pV_G = RT(1+B/V_G)$, where V_G is the molar volume of the saturated vapour and B is the second virial coefficient of the gas. In this case the corrections due to the non-ideality of the gas are:

$\eta = B/V_G - (T/V_G)(dB/dT)$ and $\epsilon = \ln(1+B/V_G) - 2B/V_G$. From eq. (II-1) and the available experimental information for the quantities in this equation it is possible to calculate the p,T relation of oxygen with a reasonable degree of accuracy. In the next section a survey of the experimental information which is required for the calculation is given, a selection from the available data is made, and a numerical formula for the p,T relation is given.

2. The calculation.

a. T h e   h e a t   o f   v a p o r i z a t i o n   o f   o x y g e n
a t   t h e   n o r m a l   b o i l i n g   p o i n t. The heat of vaporization of oxygen was measured by several investigators. When comparing the results one has to realize that, although the heat is always supplied electrically and therefore the heat input is measured in joules, the result is often given in calories. For the conversion of joules to calories different factors are used by different authors. If these conversion factors are given there is no uncertainty, but when this is not the case there remains in general an uncertainty of 0.05%.

In table II-A experimental values for the heat of vaporization of oxygen at the normal boiling point are given. Alikhanov did not mention a value for the conversion factor from calories to joules. We have assumed that in this case 1 cal = 4.185 J. For the calculation of the p,T relation the average of the experimental data for L is used. The maximum deviation from the average is 0.1%. If the value for the heat of vaporization at the normal boiling point is changed by 0.1% the p,T relation calculated from eq. (II-1) will change as is shown in fig. II-1, where temperature changes at equal pressures versus temperature are plotted.

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TABLE II-A

Experimental data for the heat of vaporization of oxygen at the normal boiling point.

Author	Year	L_1		1 cal.		L_1(J/mole)
Alt[33]	1906	50.913	cal/g	4.188	J	6823.1
Dana[34]*)	1925	1631.7	cal/mole	4.185	J	6828.7
Giauque and Johnston[35]	1929	1628.8	cal/mole	4.185	J	6816.5
Frank and Clusius[36]	1939	1630.7	cal/mole	4.1842	J	6823.2
Clusius and Konnertz[37]	1949	1630.0	cal/mole	4.1842	J	6820.2
Furukawa and McCoskey[38]	1953	6824.8	J/mole	----		6824.8
Alikhanov[39]	1956	1628.7	cal/mole	4.185	J**)	6816.1
				Average		6821.8

*) According to the recalculation of Dana's data by Giauque and Johnston.

**) Assumed factor for the conversion of calories to joules.

Alt [33], Furukawa and McCoskey [38] and Alikhanov [39] gave also results of measurements of L at other temperatures. These data are not used for the calculation of the p,T relation, but they have been used to prove the consistency of the data which are involved in the calculation (see section II-4).
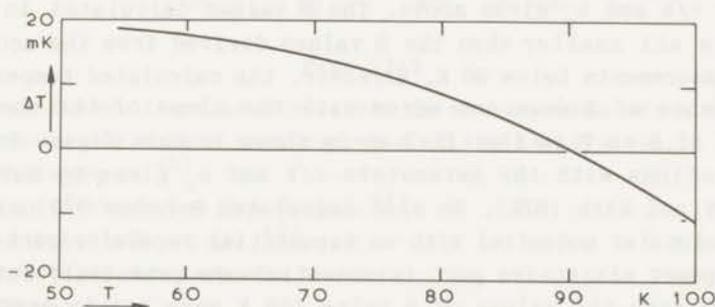
Fig. II-1

The change in the p,T relation for liquid oxygen calculated from eq. (II-1) if the heat of vaporization at the normal boiling point L_1 is changed by 0.1%. ΔT is the change in temperature at constant pressure.

b. The second virial coefficient of oxygen gas. Experimental data for the second virial coefficient of oxygen gas in the temperature range below 100 K are scarce and their inaccuracy is large. Results obtained with a double gas thermometer were given by Cath [40] and results deduced from measurements of the velocity of sound were reported by Van Itterbeek and Van Paemel [41], by Van Itterbeek et.al. [42] and by Van Lammeren [43]. At higher temperatures there is more reliable information in the results of the measurements of Cath [40] and of Nijhof and Keesom [44] below the ice-point and the values of Kuypers and Kamerlingh Onnes [45] at higher temperatures. The latter authors also corrected the results of Cath.

On the basis of this information several authors gave values for the parameters ϵ/k and b_o used in the semi-empirical calculation of the second virial coefficient with a Lennard-Jones 6-12 intermolecular potential. Hirschfelder, Curtiss and Bird [46] gave $\epsilon/k = 118$ K and $b_o = 52.26$ cm^3/mole, Woolley and Benedikt [47] gave $\epsilon/k = 116$ K and $b_o = 54.7$ cm^3/mole and Mullins, Ziegler and Kirk [48] chose in 1962 for the calculation of the p,T relation $\epsilon/k = 112$ K and $b_o = 60.84$ cm^3/mole. All these values for ϵ/k and b_o are adjusted to the measured value of B at the ice-point.

From the acoustical measurements one obtains a quantity S which is equal to $B+(RT/C_{Vi})(dB/dT)+(R^2T^2/2C_{Vi}(C_{Vi}+R))(d^2B/dT^2)$. S values can be calculated using each of the three sets of parameters ϵ/k and b_o given above. The S values calculated in this way are all smaller then the S values derived from the acoustical measurements below 90 K. Moreover, the calculated temperature dependence of S does not agree with the slope of the observed curves of S vs T in fig. II-2 as is shown in this figure for the calculations with the parameters ϵ/k and b_o given by Mullins, Ziegler and Kirk (MZK). We also calculated B below 0°C using an intermolecular potential with an exponential repulsive part and a sixth power attractive part (exponential-six potential) but also in this case the values of S below 100 K were not in agreement with the experimental data.

Therefore we decided not te use one of the well-known models to calculate the second virial coefficient of oxygen but to use the formula given by Van Lammeren [43] for the temperature range below 150 K:
$$B = -0.2702+147.83T^{-1}-311.56 \times 10^2 T^{-2}+244.12 \times 10^4 T^{-3}-71.945 \times 10^6 T^{-4}$$

l/mole, where T is the numerical value of the temperature expressed in kelvins. This formula is derived from the experimental S values obtained by Van Lammeren between 80 K and 90 K and from the experimental data for B given by Nijhoff and Keesom between 120 K and 150 K but the agreement of the calculated values for B with the experimental B values is still good at 200 K. The B values calculated with this formula are between 80 K and 120 K near to the MZK values.

In fig. II-2 the experimental S values from different authors are plotted versus temperature together with the S values calculated from the formula of Van Lammeren and those calculated from the formula for B given by MZK. Van Itterbeek et. al. gave their measured S values only in a graph. The line that they drew through their experimental points is given in fig. II-2. The scattering of their experimental points is a few percent. C_{vi}/R was taken equal to 5/2 for the calculation of S.
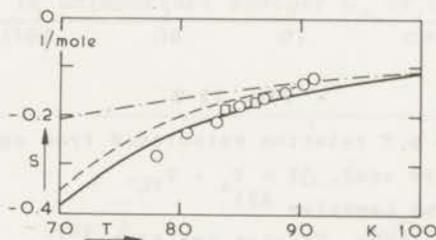
Fig. II-2

The significant function S involved in measurements of the velocity of sound for oxygen as a function of the temperature.

☐ Van Lammeren [43)]
○ Van Itterbeek and Van Paemel [41)]
── Van Itterbeek et al. [42)]
--- Formula of Van Lammeren
-.- MZK values.

In the correction terms η and ϵ in eq. (II-1) also V_G appears. V_G was calculated by iterative solution of the equation of state using values for p and T which were taken from a provisional p,T relation. For this provisional p,T relation the representation of the calculated p,T data from MZK given in ref. 49 was used, but

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the constant term was changed from 28.888394 to 28.887477 to obtain p = 760 mm Hg at $0°C$ and at standard gravity for T = 90.188 K (the value recommended for the boiling point of oxygen by the C.C.T. in 1967).

The changes of the T values calculated from eq. (II-1) at equal pressures, when the B values calculated with the parameters given by MZK and by Hirschfelder et.al. are used instead of those of Van Lammeren are shown in fig. II-3.
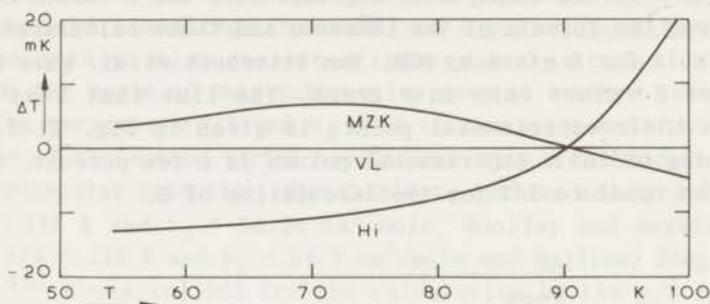
Fig. II-3

The change in the p,T relation calculated from eq.(II-1) if different B values are used. $\Delta T = T_x - T_{VL}$.
VL   B values of Van Lammeren [43]
MZK B values of Mullins, Ziegler and Kirk [48]
Hi   B values of Hirschfelder, Curtiss and Bird [46].

Van Itterbeek and Van Paemel gave also values for the third virial coefficient of oxygen. The corrections on the p,T relation due to this third virial coefficient, however, are much smaller than the uncertainty in the corrections due to the second virial coefficient and therefore no third virial coefficient has been introduced in our calculations.

c. The heat capacities of the vapour and of the liquid. The molar heat capacity at constant volume of oxygen gas in the ideal gas state, calculated by Woolley [50] from spectroscopic data, were represented for the temperature range between 50 K and 100 K by the formula:
$C_{Vi} = R(2.4958 + 0.0003\,T + 0.35\,T^{-1})$, R = 8.3143 J/mole K.

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The heat capacity of liquid oxygen was measured in 1929 by Giauque and Johnston [35] and by Clusius [51]. The results between 56 K and 73 K obtained by Clusius with two different vessels show a scattering of 4%. The data of Giauque and Johnston between 56 K and 90 K show a scattering of not more than 0.2%. In both papers the measured quantity is called C_p but according to the method of measurement one may assume that the measured quantity is the heat capacity at saturation pressure C_s. From thermodynamics it can be derived that $C_p - C_s = T(dV_L/dT)_s (dp/dT)_s - T(\partial V_L/\partial p)_T (dp/dT)_s^2$, where s indicates saturation. Using $(dp/dT)_s$ from a provisional p,T relation, $(dV_L/dT)_s$ from V_L at saturation (see section II-2d) and $(\partial V_L/\partial p)_T$ according to the calculations of David and Harmann [52,53] for temperatures higher than 88 K, $C_p - C_s$ was calculated. The difference $C_p - C_s$ is below 83 K smaller than 0.1% of C_s, at 90 K it is 0.2% of C_s and at 100 K it is 0.6% of C_s. Since the heat capacity was measured only below 90 K it must be extrapolated to 100 K. This extrapolation introduces such an uncertainty that it is unimportant whether C_p or C_s was the really measured quantity.
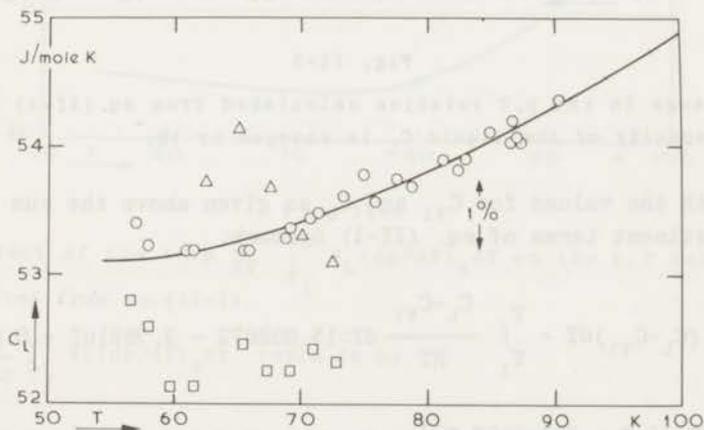
Fig. II-4

The molar heat capacity of liquid oxygen at saturation.
  ○ Giauque and Johnston [35]
  □,△ Clusius [51]
  ——— Smoothed representation.

We chose for the calculation of the p,T relation the following representation of the data of Giauque and Johnston:

$C_s = R(5.280+0.01019\ T+30.15\ T^{-1})$.

The form of the formula for C_s (or C_L) was chosen in this way in order to keep the change of the slope of the C_s versus T curve small in the extrapolated part. The experimental data and the smoothed values are shown in fig. II-4.

It is not easy to estimate the inaccuracy in the heat capacity of the liquid but it is probably less than 1%. The effect on the calculated p,T relation of a change of 1% in the heat capacity of the liquid over the whole temperature range is shown in fig. II-5.
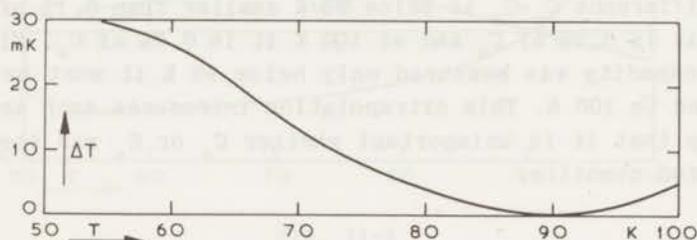
Fig. II-5

The change in the p,T relation calculated from eq.(II-1) if the heat capacity of the liquid C_L is changed by 1%.

With the values for C_{Vi} and C_L as given above the sum of the two pertinent terms of eq. (II-1) becomes:

$$\frac{1}{RT}\int_{T_1}^{T}(C_L-C_{Vi})dT\ -\ \int_{T_1}^{T}\frac{C_L-C_{Vi}}{RT}\ dT=15.908672\ -\ 2.785\ln T\ -\ 0.00508T+$$

$$+\ 29.80T^{-1}\ln T\ -\ 396.8502\ T^{-1}.$$

d. The molar volume of the liquid at saturation pressure. The molar volume of the liquid at saturation pressure V_L was calculated for all integral values of T between 55 K and 100 K from an empirical equation

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given by Scott [54]. The results were represented by the second degree polynominal:

$V_L = (23.290 - 0.0124 \, T + 0.000725 \, T^2) \, cm^3/mole$. Using this polynominal for V_L and a provisional p,T relation, the small steps $\int_T^{T+1} \frac{V_L}{R} (\frac{dp}{dT})_s dT$ were approximated by $\frac{(V_L)_{T+0.5}}{R} (p_{T+1} - p_T)$ from

T = 54 K to T = 99 K. From these steps and from

$((V_L)_{90.09 \, K}/R)(p_{90.188 \, K} - p_{90 \, K})$ the values of the term

$(1/RT) \int_{T_1}^{T} V_L (dp/dT)_s \, dT$ were obtained for all integral values

of T from 54 K to 100 K. This method of calculation is accurate enough since the total influence of this term on ln p is, below 95 K, smaller than the equivalent of 25 m K (see fig. II-6). It is equivalent to 63 mK at 100 K.
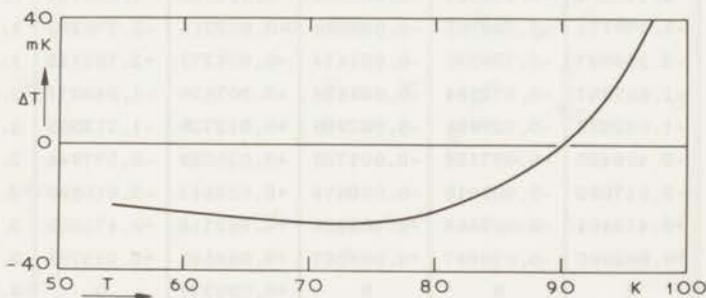
Fig. II-6

The effect of the term $\frac{1}{RT} \int_{T_1}^{T} V_L (dp/dT)_s dT$ on the p,T relation calculated from eq. (II-1).

$$\Delta T = \frac{1}{RT} \int_{T_1}^{T} VL(dp/dT)_s dT \quad (dT/d \ln p)$$

e. Representation of the p,T relation. Using the data which are specified above and R=8.3143 J/K mole and taking T_1, at a pressure of 760 mm Hg at 0°C and standard gravity, equal to 90.188 K according to the recommendation of the C.C.T. of 1967 ln p/p_1 and ^{10}log p were calculated at all integral values of T from 54 K to 100 K. An abstract of this calculation is given in table II-B where:

$$A = \frac{L_1}{RT_1} - 1 - \eta_1, \quad -I_1 + I_2 = -\int_{T_1}^{T} \frac{(C_L - C_{Vi})}{RT} \, dT + \frac{1}{RT} \int_{T_1}^{T} (C_L - C_{Vi}) \, dT \text{ and}$$

$$I_3 = \frac{1}{RT} \int_{T_1}^{T} V_L \left(\frac{dp}{dT}\right)_s dT.$$

TABLE II-B

Abstract of the calculation of the p,T relation for liquid oxygen from eq. (II-1).

T(K)	$A(1-T_1/T)$	$-I_1+I_2$	I_3	ϵ	$\ln(p/p_1)$	$^{10}\log p$
55	-5.235002	-0.575364	-0.006036	+0.000420	-6.340915	0.126989
60	-4.116878	-0.379521	-0.005505	+0.001036	-4.938791	0.735924
65	-3.170774	-0.238785	-0.005006	+0.002214	-3.770232	1.243423
70	-2.359827	-0.139630	-0.004474	+0.004275	+2.783428	1.671986
75	-1.657007	-0.072384	-0.003826	+0.007626	-1.940371	2.038122
80	-1.042039	-0.029994	-0.002960	+0.012729	-1.212505	2.354230
85	-0.499420	-0.007196	-0.001755	+0.020039	-0.577948	2.629814
90	-0.017092	-0.000010	-0.000074	+0.029942	-0.019690	2.872263
95	+0.414464	-0.005368	+0.002226	+0.042718	+0.475650	3.087386
100	+0.802865	-0.020887	+0.005297	+0.058523	+0.918701	3.279801
90.188	0	0	0	+0.030370	0	2.880814

The calculated values for $^{10}\log p$ were represented by an equation of the form:

$$^{10}\log p = A + BT^{-1} + C\,^{10}\log T + DT + ET^2$$

If p is expressed in mm Hg at $0°C$ and standard gravity and T is the numerical value of the temperature expressed in kelvins. The values for the constants are:
$A = 9.191084$, $B = -449.94111$, $C = 0.126660$, $D = -0.02424499$ and $E = 75.9321 \times 10^{-6}$. The equation represents the calculated values with a standard deviation of 0.18 mK and a maximum deviation of 0.36 mK. Temperatures that are calculated from vapour pressures with this formula are denoted T_{pc}.

3. Comparison of the calculated p,T relation with results of experiments and with results of other calculations.

There are many measurements of the vapour pressure of liquid oxygen as a function of temperature which can be compared with the calculated p,T relation given in the foregoing section. In fig. II-7 and fig. II-8 differences between temperatures T_{pc} and temperatures measured during the last sixty years are plotted.
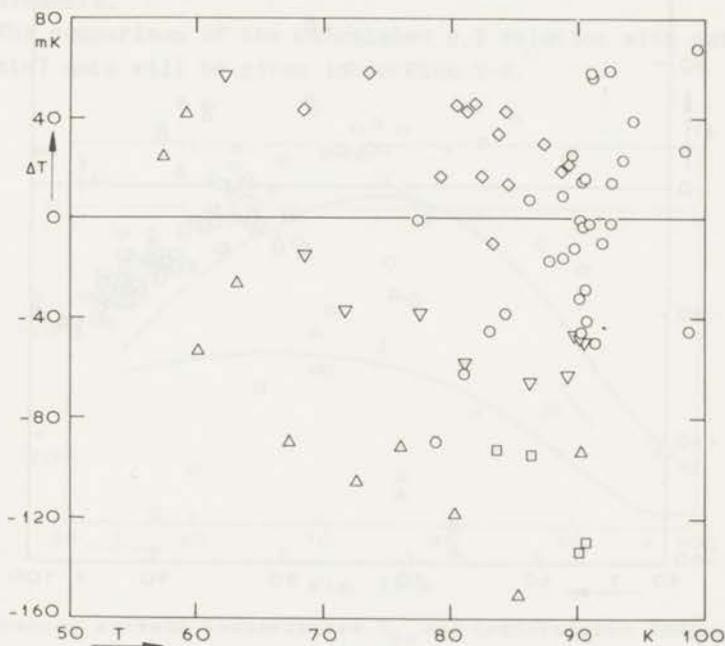
Fig. II-7

Differences between temperatures T_{pc} deduced from measured vapour pressures of liquid oxygen and temperatures T_m measured with cali-brated thermometers as obtained by different authors. $\triangle T = T_m - T_{pc}$.

☐ Kamerlingh Onnes and Braak [4]
△ Von Siemens [55]
▽ Cath [56]
◇ Henning and Heuse [57]
o Dodge and Davis [58]

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The distribution of the data over two figures is made for clearness.

The results of Hoge [61] were recalculated from the NBS-1939 scale and the IPTS-1948 to the CCT-64 scale (see section 1-2) in order to make a better comparison with our own experiments possible (see section V-3a).
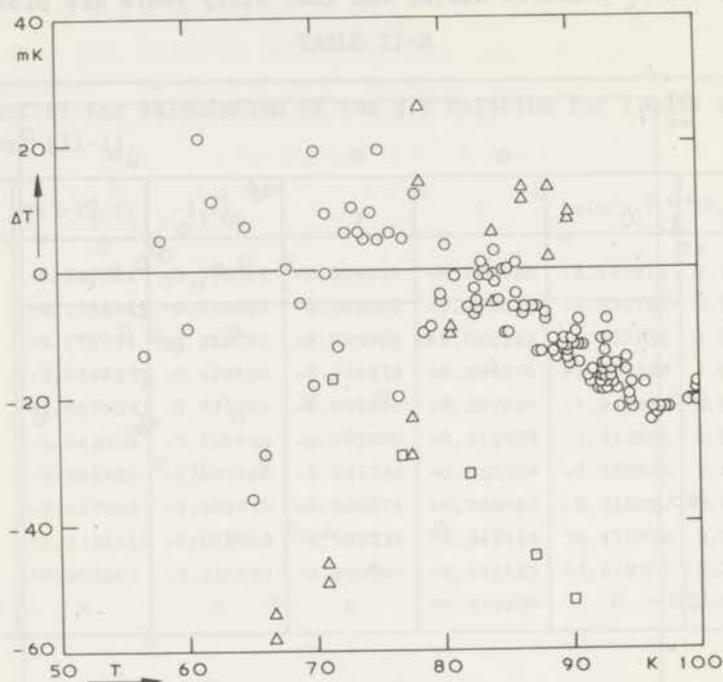
Fig. II-8

Differences between temperatures T_{pc} deduced from measured vapour pressures of liquid oxygen and temperatures T_m measured with calibrated thermometers as obtained by different authors. $\Delta T = T_m - T_{pc}$.

□ Giauque, Johnston and Kelley [59]
△ Henning and Otto [60]
o Hoge [61]

Very reproducible measurements of the vapour pressure of oxygen as a function of temperature were performed by Mochizuki, Sawada and Takahashi [62] for pressures between 660 mm Hg (89 K)

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and 860 mm Hg (91.5 K). The temperature was measured with platinum thermometers on the IPTS-1948. The results were represented in a formula giving t_{int} as a function of $(p-p_1)$.

The differences between the measured and the calculated temperatures as given in fig. II-7 and fig. II-8, are probably mainly due to errors in the calibration of the thermometers that are used for the measurements, which, in turn, are mainly caused by errors in the temperature measurements with the gas thermometer. The scattering of the points is the largest for the older measurements.

The comparison of the calculated p,T relation with our experimental data will be given in section V-3.
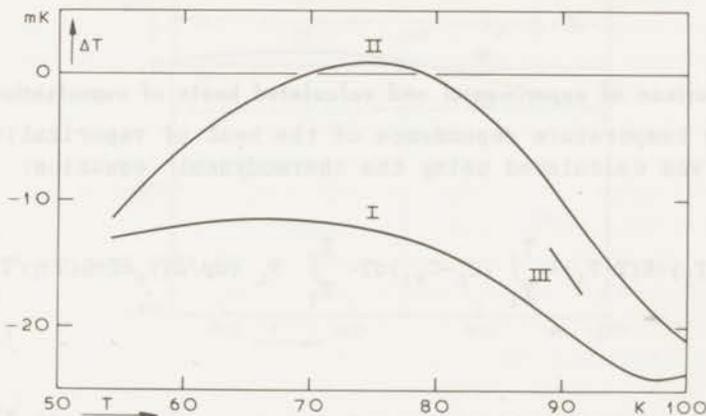
Fig. II-9

Differences between temperatures T_{pc} and temperatures deduced from p,T relations of different authors.

I T_{MZK}(ref. 48) - T_{pc}
II T_{MMD}(ref. 49, eq.(4))- T_{pc}
III T_{MST}(ref. 62, recalculated on the CCT-64 scale) - T_{pc}

In fig. II-9 our calculated p,T relation (T_{pc}) is compared with the p,T relation calculated by Mullins, Ziegler and Kirk [46] (T_{MZK}), who collected the experimental data used in the calculation from nearly the same sources as we did but who used 90.168 K for the boiling point, with the p,T relation given in table IX of our previous paper on the vapour pressure of liquid

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oxygen [49] (T_{MMD}) and with the representation of the results of Mochizuki, Sawada and Takahashi (T_{MST}) recalculated to the CCT-64 scale.

The results of our calculation are in very good agreement with the results of the calculation of MZK. The differences between T_{pc} and temperatures calculated from the p,T relation of our previous paper, which relation is, according to our measurements, in close agreement with the CCT-64 scale, might be explained from the uncertainty in the thermodynamic data but these differences may also be partly due to deviations of the CCT-64 scale from the thermodynamic temperature. The latter deviations may be expected to be of the same order of magnitude as the differences between the national scales and the CCT-64 scale [28].

4. Comparison of experimental and calculated heats of vaporization.

The temperature dependence of the heat of vaporization of oxygen was calculated using the thermodynamic equation:

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

$$(II-2)$$

The derivation of this formula was given by Van Dijk [32] in his paper on the derivation of eq. (II-1). Values for the heat of vaporization which were calculated using eq. (II-2) are given in table II-C at all integral values of T between 55 K and 100 K.

The calculated heats of vaporization can be compared with the measured values of Furukawa and McCoskey [38] and with those of Alikhanov [39] and with the calculated values of MZK [48]. In fig. II-10 the differences are shown. Also the other experimental data for L mentiones in section II-2a are plotted in fig. II-10.

The differences are nearly all within 0.1% except for the data of Alikhanov for which the differences with the calculated L values are beyond the estimated limits of accuracy.

The experimental data of Alt show a scattering of 1% but the average of his results is in good agreement with the other data.

The agreement of the calculated heats of vaporization with the experimental values of Furukawa and McCoskey is within the estimated limits of accuracy of the experimental points. This shows the consistency of the data which are used in the calculation.
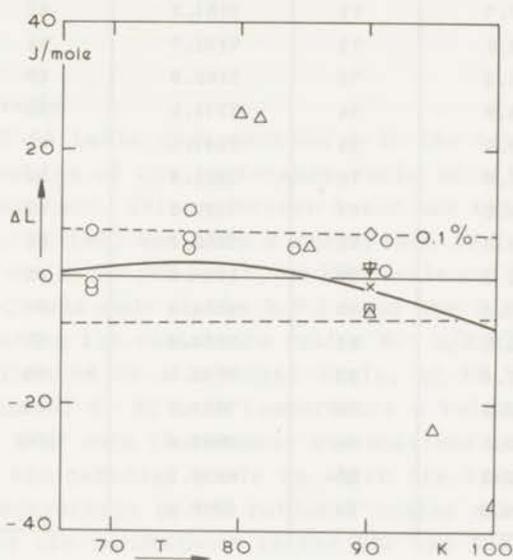
Fig. II-10

Differences between values for the heat of vaporization of liquid oxygen calculated from eq. (II-2) (L_c) and values for the heat of vaporization obtained by other authors from experiments or calculations (L_x). $\Delta L = L_x - L_c$.

+   Alt [33]   (exp.)
◇   Dana [34]   (exp.)
□   Giauque and Johnston [35]   (exp.)
▽   Frank and Clusius [36]   (exp.)
×   Clusius and Konnertz [37]   (exp.)
o   Furukawa and McCoskey [38]   (exp.)
△   Alikhanov [39]   (exp.)
—— Mullins, Ziegler and Kirk [48] (calc.)

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TABLE II-C

The heat of vaporization of liquid oxygen between 55 K and 100 K as calculated using eq. (II-2).

T(K)	L(J/mole)	T(K)	L(J/mole)	T(K)	L(K/mole)
55	7747.7	71	7351.3	87	6917.3
56	7723.5	72	7325.7	88	6887.8
57	7699.2	73	7299.9	89	6857.9
58	7674.9	74	7273.9	90	6827.6
59	7650.5	75	7247.8	91	6796.8
60	7626.0	76	7221.5	92	6765.5
61	7601.5	77	7195.0	93	6733.8
62	7576.9	78	7168.3	94	6701.6
63	7552.2	79	7141.4	95	6668.9
64	7527.4	80	7114.3	96	6635.7
65	7502.5	81	7087.0	97	6602.0
66	7477.6	82	7059.5	98	6567.8
67	7452.6	83	7031.7	99	6533.1
68	7427.5	84	7003.6	100	6497.8
69	7402.2	85	6975.2		
70	7376.8	86	6946.4		

CHAPTER III

RECENT TEMPERATURE SCALES FOR PLATINUM THERMOMETERS

1. The CCT—64 scale

In the CCT-64 table (see section I-2) the temperature is
given as a function of the resistance ratio of a hypothetical
"average thermometer". This reference table was obtained in the
following way: In 1962 and 1963 a comparison of four national
scales (the NBS scale, the PSU scale, the PRMI scale and the NPL scale,
see section I-2) was made at the N.P.L. and the P.R.M.I. [22,23,
24,25] by comparing the resistance ratios $W(= R/R(0°C))$ of ther-
mometers, calibrated on a national scale, at 66 temperatures
between 10 K and 91 K. At each temperature a value for the re-
sistance ratio W of each thermometer was obtained and a tempera-
ture value on the national scale on which the thermometer was
calibrated. Temperatures on the national scales were reduced in
order to obtain the recommended values for the temperatures at
the boiling points of oxygen and hydrogen. The reduction was made
by using the values for these boiling points given by each insti-
tute on its own scale (the so-called "declared values") and the
values for these points that were recommended provisionally by
the C.C.T. in 1962. These values are given in table III-A.

TABLE III-A

The boiling points of oxygen and hydrogen on the four national
scales and those recommended by the C.C.T. in 1962.

	NBS (1939)	PSU	PRMI	NPL	CCT 1962
n-H_2	20.392^5 K	20.365 K	20.394 K	20.387^5 K	20.384 K
O_2	90.190 K	90.151 K	90.199 K	90.180 K	90.170 K

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The reduction was linear between these fixed points and in the extrapolated parts. In this way a better agreement between the scales was obtained. The formulae from which the reduced temperatures between 10 K and 92 K may be calculated are:

$$T_{NBS-1939, red.} = T_{NBS-1939} - 0.00514 \text{ K} - 0.0001648 \text{ T}$$
$$T_{PSU, red.} = T_{PSU} + 0.01900 \text{ K}$$
$$T_{PRMI, red.} = T_{PRMI} - 0.00445 \text{ K} - 0.0002723 \text{ T}$$
$$T_{NPL, red.} = T_{NPL} - 0.00160 \text{ K} - 0.0000931 \text{ T}$$

After the reduction the results were expressed as W values for the thermometers and corresponding reduced temperatures. The reduced temperatures obtained for each of the four scales were averaged at each of the 66 points. The equation giving the average reduced temperature is: $\overline{T}_{nr} = \frac{1}{4} (T_{NBS, red.} + T_{PSU, red.} + T_{PRMI, red.} + T_{NPL, red.})$. The W values were averaged in such a way that the two thermometers of P.S.U. and the one remaining thermometer of N.B.S. together got the same weight as the two thermometers of N.P.L. and as the one remaining thermometer of P.R.M.I. because both the P.S.U. thermometers and the N.B.S. thermometer were made from platinum from the same source. In this way each of the three kinds of pure platinum was given the same weight. The equation giving the average resistance ratio is:

$$\overline{W} = \frac{1}{12} (W_{PSU3} + W_{PSU4} + 2W_{NBS2} + 2W_{NPL2} + 2W_{NPL3} + 4W_{T2}).$$

The average reduced temperatures $\overline{T}_{nr}$ were represented at the P.R.M.I. by a smooth function of the average resistance ratio in the following way: $\overline{T}_{nr} = \sum_{n=0}^{11} A_n (\log \overline{W})^n$. The constants A_n could
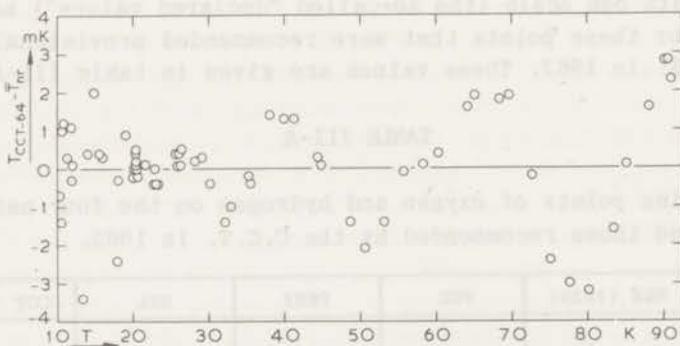
Fig. III-1

Differences between T_{CCT-64} and $\overline{T}_{nr}$ from 10 K to 91 K.

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be determined by a least squares analysis of the 66 data for $\overline{W}$ and $\overline{T}_{nr}$. The values of T calculated from this equation differ slightly from the $\overline{T}_{nr}$ values obtained directly at the 66 experimental points. These differences (the so-called "smoothing corrections") were given by Orlova et al. [24] and are shown in fig. III-1. A table, known as the B1 table, was calculated from the equation. In this table the temperature is given as a function of W. The part of the CCT-64 table between 12 K and 90.24 K is taken from the B1 table. At higher temperatures the CCT-64 table is a smooth representation by Barber and Hayes [26] of the results of measurements with platinum thermometers and a gas thermometer of Barber and Miss Horsford [27]. The T(W) function of Barber and Hayes and its first derivative join at 90.24 K continuously to the data of the B1 table.

The W values of the thermometers which were used for the comparison of the scales are directly related to the values of $\overline{W}$ at the 66 points. Values of W-$\overline{W}$ at intermediate temperatures may be obtained by graphical interpolation with a smooth curve through the measured points. At each temperature in the temperature range under consideration the W values of a number of platinum thermometers can be related in this way to a value of $\overline{W}$ and $\overline{W}$ is related to a temperature value by the CCT-64 table. Thus these platinum thermometers and the CCT-64 table constitute a temperature scale. This scale is called the CCT-64(MDD) scale and temperatures on this scale are denoted T_{CCT-64}. The reason for the addition "(MDD)" is explained in section I-2 but the addition will be omitted from now on because here only the CCT-64(MDD) scale is used.

Each of the thermometers was calibrated previously on one of the national scales. From these calibration data a value for W of a thermometer could be obtained at any temperature on a national scale and, using the results of the scale comparions, also a value for $\overline{W}$ and for T_{CCT-64}. In this way we calculated in 1965 the differences between the national scales and the CCT-64 scale. The results of these calculations are given in ref. 28 and in section III-3.

For the representation of the results of our experiments it was possible to use the CCT-64 scale directly because we had the opportunity to use in a part of our measurements the thermometers that were used for the scale comparisons.

2. The proposed IPTS-1968

According to the recommendations of the C.C.T. drafted in September 1967 the International Practical Temperature Scale of 1968 (IPTS-1968, see section I-2) will be based below 273.15 K on fixed points and on the use of platinum resistance thermometers. The resistance ratio W of a platinum thermometer has to be determined at a number of fixed points. To obtain temperature values from measured resistance ratios at intermediate temperatures a reference table of T as a function of W will be used together with defined interpolation formulae for the difference between W given in the reference table and W of the thermometer.

The formulae provisionally adopted by the C.C.T. in September 1967 for the interpolation of the differences between the W values given in the reference table and the W values of a thermometer are:

1. For the temperature range between $0°C$ and the boiling point of oxygen: $\Delta W = a_1 t + b_1 t^3(t-100°C)$, where $t = T -273.15$ K. The constants must be determined from the values of ΔW at the steam-point ($t=100°C$) and at the boiling point of oxygen ($t= -182.962°C$).

2. For the temperature range between the boiling point and the triple point of oxygen: $\Delta W = a_2 + b_2 T + c_2 T^2$.
   The constants must be determined from the values of ΔW at the O_2 boiling point ($T=90.188$ K) and at the O_2 triple point ($T=54.361$ K) and from $d\Delta W/dT$ at 90.188 K as obtained from the interpolation formula for the higher adjacent temperature range.

3. For the temperature range between the boiling point and the triple point of e-hydrogen: $\Delta W = a_3 + b_3 T + c_3 T^2$.
   The constants must be determined from the values of ΔW at the e-H_2 boiling point ($T=20.280$ K), at the point where the vapour pressure of e-H_2 is 25/76 atm ($T=17.0422$ K) and at the e-H_2 triple point ($T=13.810$ K).

4. For the temperature range between the triple point of oxygen and the boiling point of e-hydrogen: $\Delta W = a_4 + b_4 T + c_4 T^2 + d_4 T^3$.
   The constants must be determined from the values of ΔW at the O_2 triple point ($T=54.361$ K) and at the e-H_2 boiling point

(T=20.280 K) and from $d\triangle W/dT$ at 54.361 K and at 20.280 K as obtained from the interpolation formulae for the higher and the lower adjacent ranges.

This interpolation method is chosen by the C.C.T. from a number of possibilities, partly on the basis of the results of our comparison of different methods for the interpolation of W differences These results are given in section VI-1.

In February 1968 Preston-Thomas of the N.R.C. proposed to use also the neon boiling point (27 K) as a calibration point and to change the interpolation procedure below 54 K. The addition of this fixed point improves the reproducibility of the scale for thermometers of different quality or origin.

In May 1968 at a meeting of a small committee of the C.C.T., the so-called editorial committee for the text of the IPTS-1968, it was decided to adopt the neon boiling point as a primary fixed point and to define the interpolation of $\triangle W$ values below 54 K as follows.

For the temperature range between the triple point of oxygen and the boiling point of e-hydrogen: $\triangle W = a_3 + b_3 T + c_3 T^2 + d_3 T^3$.
The constants must be determined from the values of $\triangle W$ at the O_2 triple point (T=54.361 K), the Ne boiling point (T=27.102 K) and the e-H_2 boiling point (T=20.280 K) and from $d\triangle \dot{W}/dT$ at 54.361 K as obtained from the interpolation formula for the higher adjacent range.

For the temperature range between the boiling point and the triple point of e-hydrogen: $\triangle W = a_4 + b_4 T + c_4 T^2 + d_4 T^3$
The constants must be determined from the values of $\triangle W$ at the e-H_2 boiling point (T=20.280 K), at the point where the vapour pressure of e-H_2 is 25/76 atm (T=17.0422 K) and at the e-H_2 triple point (T=13.810 K) and from $d\triangle W/dT$ at 20.280 K as obtained from the interpolation formula for the higher adjacent range.

The differences between the CCT-64 scale and the IPTS-1968 can be calculated when the values of the fixed points on the CCT-64 scale are known and the reference table to be used for the IPTS-1968 is available.

From information from different sources and from our own measurements the "best values" for the fixed points on the CCT-64 scale could be chosen. In table III-B these values and the corresponding values of $\overline{W}$ from the CCT-64 table are given together with the values of T_{68} at the fixed points according to the recom-

mendations of the C.C.T. [63] (for the neon boiling point $T_{68} =$ 27.102 K was recommended in May 1968).

TABLE III-B

Values for the fixed points on the CCT-64 scale, corresponding values for $\overline{W}$ from the CCT-64 table and the recommended values for T_{68}.

Fixed point	T_{CCT-64} (K)	$\overline{W}$	T_{68} (K)
steam point	373.15	1.392620	373.15
"ice-point"	273.15	1.0000000	273.15
O_2 b.p.	90.1727	0.2438108	90.188
O_2 tr.p.	54.352	0.0919686	54.361
Ne b.p.	27.096	0.0122122	27.102
$e-H_2$ b.p.	20.275	0.0044846	20.28
$e-H_2$ p=25/76 atm	17.0399	0.0025337	17.0422
$e-H_2$ tr.p.	13.825	0.0014118	13.81

The way in which T_{CCT-64} at the fixed points of oxygen and hydrogen was obtained will be discussed in chapter V. The value for T_{CCT-64} at the neon boiling point was taken from the results of measurements of Grilly [64] ($T_{NBS-1955} = 27.092$ K) and Furukawa [65] ($T_{NBS-1955} = 27.098$ K). The average of these values corresponds to $T_{CCT-64} = 27.096$ K (see section III-3). This value is within the limits of accuracy also in agreement with the value 27.11 K obtained by Haantjes [66].

As was shown in ref. 67 $\overline{W}$ at 100°C may be taken equal to 1.392620.

In September 1967 it was decided that a new reference table should be calculated for the IPTS-1968, mainly because results of accurate measurements with a helium gas thermometer and platinum thermometers between 90 K and 100°C became available at the N.R.C. [68]. Below 90 K the results of the comparison of the national scales had to be reduced to the new values for the boiling points of oxygen and hydrogen and above 90 K the W values of the thermometers which were calibrated at the N.R.C. had to be reduced in order to obtain agreement with $\overline{W}$ at 90 K. On the basis of the data thus obtained a smooth T(W) function for an "average

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thermometer" had to be computed. Preston-Thomas and Bedford of the N.R.C. offered to do this rather extensive work.

The outline of the computation given above leaves several problems to be solved. The first is, that for all thermometers, that were used to define the upper part of the table, only platinum from the same source was used, while for the lower part the W values of thermometers from different sources were averaged. This can give rise to difficulties in connecting the two parts of the table and to somewhat odd-shaped ΔW curves above 90 K for thermometers from other manufacturers. The second is, that the results of the scale comparisons were reduced to the new values for the boiling points of oxygen and hydrogen only and not to the new values of the triple points. This can give rise to odd-shaped ΔW curves for all real thermometers. Additional difficulties are, that the "average reduced temperature scale" (see section III-1) may have short range curvature changes since none of the four national scales on which it is based is very well smoothed and that the slope of the "average reduced scale" at 90 K differs from the slope of the N.R.C. gas thermometer scale.

Therefore it is not surprising that some inconveniences existed in the result of a first computation which was in very good agreement with the experimental data. The most important inconvenience was, that d^2W/dT^2 was not as smooth as desirable between 80 K and 120 K. Other points were, that the curves for the differences between the W values of the table and W values of a real thermometer were not in very good agreement with curves for the W differences of real thermometers, and that this table gave rise to a discontinuity in d^2W/dT^2 at the ice point.

We computed by hand a skeleton table in which most of the inconveniences were solved and also at the N.R.C. some alternative tables were computed, but in May 1968, when the editorial committee had a meeting to complete the text of the IPTS-1968, a final decision about the reference table could not yet be attained.

In the text of the IPTS-1968 also the relations between the vapour pressures of oxygen, neon and hydrogen and T_{68} must be given. These relations are required because it is in general not possible to realize an equilibrium state between two phases at exactly the prescribed pressure and because it is convenient that temperatures, determined by a vapour pressure thermometer, are

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in agreement with temperatures T_{68} as determined by a platinum thermometer. For oxygen this p,T relation may be calculated from the relation between p and T_{CCT-64} as given in section V-3a and the differences between T_{68} and T_{CCT-64} as soon as the reference table for the IPTS-1968 is ready. The p,T relation of liquid neon may be based on the results of Grilly [64]. For e-H_2 is taken the relation calculated by Ter Harmsel (see section V-2d).

3. Differences between temperature scales for platinum thermometers.

In this section a table is given for the differences between the principal temperature scales for platinum thermometers for the temperature range below the boiling point of oxygen.

The way in which the differences between the CCT-64 scale and the temperature scales of the N.B.S., the P.S.U., the P.R.M.I. and the N.P.L. were calculated is explained in section III-1. The results of this calculation were reported earlier to the C.C.T. [28].

The differences between the scales are given in table III-C and shown in fig. III-2.
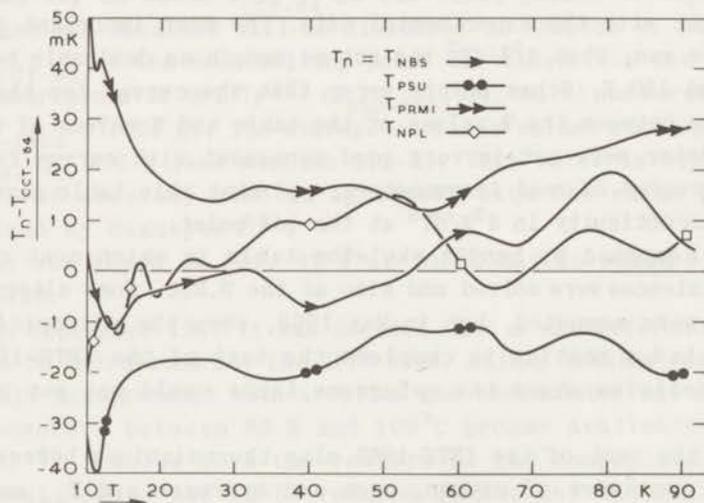
Fig. III-2

Differences between the national scales and the CCT-64 scale from 10 K to 91 K.

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TABLE III-C
Scale differences $T_n - T_{CCT-64}$ in mK

T_n / n	NBS-1955	PSU	PRMI	NPL
10.0	4.0	- 32	58.8	- 21.6
.1	3.0		56.0	- 21.0
.2	2.2		53.3	- 20.3
.3	1.7		50.6	- 19.5
.4	1.0		48.2	- 18.8
.5	0.3	- 36	46.1	- 18.1
.6	- 0.4		44.4	- 17.4
.7	- 1.1		43.0	- 16.6
.8	- 1.8		41.9	- 15.9
.9	- 2.4		41.0	- 15.1
11.0	- 3.0	- 39.5	40.4	- 14.4
.1	- 3.6		39.9	- 13.6
.2	- 4.2		39.5	- 12.9
.3	- 4.7		39.5	- 12.1
.4	- 5.2		39.9	- 11.4
.5	- 5.8	- 40	40.7	- 10.7
.6	- 6.3		41.4	- 10.2
.7	- 6.8		42.0	- 9.8
.8	- 7.2		42.2	- 9.5
.9	- 7.7		42.0	- 9.2
12.0	- 8.1	- 36	41.5	- 9.0
.1	- 8.5		40.8	- 8.8
.2	- 8.9		40.2	- 8.6
.3	- 9.3		39.6	- 8.6
.4	- 9.6		39.0	- 8.5
.5	- 10.0	- 31	38.5	- 8.6
.6	- 10.3		38.0	- 8.6
.7	- 10.5		37.6	- 8.8
.8	- 10.8		37.2	- 9.0
.9	- 11.0		36.9	- 9.2
13.0	- 11.2	- 28	36.5	- 9.4
.1	- 11.4		36.2	- 9.6
.2	- 11.5		35.9	- 9.9

T_n / n	NBS-1955	PSU	PRMI	NPL
13.3	- 11.6		35.6	- 10.3
.4	- 11.6		35.3	- 10.6
.5	- 11.7	- 26	35.0	- 11.0
.6	- 11.6		34.7	- 11.4
.7	- 11.6		34.4	- 11.7
.8	- 11.5		34.1	- 12.0
.9	- 11.4		33.7	- 12.3
14.0	- 11.3	- 24	33.4	- 12.5
.1	- 11.1		33.0	- 12.6
.2	- 11.0		32.6	- 12.6
.3	- 10.8		32.1	- 12.6
.4	- 10.6		31.7	- 12.6
.5	- 10.4	- 23	31.2	- 12.5
.6	- 10.2		30.7	- 12.3
.7	- 10.0		30.2	- 12.0
.8	- 9.8		29.8	- 11.7
.9	- 9.5		29.3	- 11.3
15.0	- 9.2	- 21.6	28.7	- 10.9
.1	- 9.0	- 21.4	28.3	- 10.4
.2	- 8.7	- 21.2	28.0	- 9.8
.3	- 8.4	- 21.0	27.6	- 9.2
.4	- 8.2	- 20.9	27.2	- 8.5
.5	- 7.9	- 20.8	26.9	- 7.7
.6	- 7.6	- 20.7	26.5	- 6.9
.7	- 7.3	- 20.5	26.2	- 6.0
.8	- 7.1	- 20.4	25.9	- 5.2
.9	- 6.9	- 20.2	25.7	- 4.3
16.0	- 6.7	- 20.1	25.4	- 3.6
.1	- 6.4	- 20.0	25.1	- 2.9
.2	- 6.2	- 19.9	24.8	- 2.1
.3	- 6.0	- 19.8	24.5	- 1.4
.4	- 5.8	- 19.7	24.3	- 0.8
.5	- 5.7	- 19.6	24.0	- 0.2

TABLE III-C (continued)

$$T_n - T_{CCT-64} \text{ in mK}$$

T_n \ n	NBS-1955	PSU	PRMI	NPL	T_n \ n	NBS-1955	PSU	PRMI	NPL
16.6	- 5.5	- 19.5	23.7	0.3	19.9	- 4.0	- 17.9	18.2	- 4.9
.7	- 5.4	- 19.4	23.5	0.8	20.0	- 4.0	- 17.9	18.0	- 4.7
.8	- 5.2	- 19.4	23.3	1.3	.1	- 3.9	- 17.8	17.9	- 4.5
.9	- 5.1	- 19.3	23.0	1.6	.2	- 3.8	- 17.8	17.8	- 4.3
17.0	- 5.0	- 19.2	22.8	1.9	.3	- 3.8	- 17.8	17.7	- 4.1
.1	- 4.9	- 19.1	22.6	2.0	.4	- 3.7	- 17.8	17.6	- 3.8
.2	- 4.8	- 19.0	22.4	2.0	.5	- 3.6	- 17.8	17.5	- 3.6
.3	- 4.7	- 19.0	22.2	2.0	.6	- 3.6	- 17.7	17.4	- 3.3
.4	- 4.6	- 18.9	22.0	2.0	.7	- 3.6	- 17.7	17.3	- 3.0
.5	- 4.6	- 18.8	21.8	1.8	.8	- 3.5	- 17.7	17.2	- 2.7
.6	- 4.5	- 18.8	21.6	1.5	.9	- 3.4	- 17.6	17.2	- 2.4
.7	- 4.4	- 18.7	21.4	1.2	21.0	- 3.4	- 17.6	17.1	- 2.1
.8	- 4.4	- 18.7	21.2	0.8	.5	- 3.1	- 17.6	16.7	- 0.9
.9	- 4.4	- 18.6	21.0	0.3	22.0	- 2.8	- 17.5	16.3	0.2
18.0	- 4.4	- 18.6	20.8	- 0.2	.5	- 2.6	- 17.4	16.0	1.1
.1	- 4.4	- 18.6	20.6	- 0.8	23.0	- 2.4	- 17.4	15.6	1.7
.2	- 4.4	- 18.5	20.5	- 1.4	.5	- 2.2	- 17.4	15.4	2.0
.3	- 4.4	- 18.5	20.3	- 1.9	24.0	- 2.1	- 17.4	15.1	2.2
.4	- 4.4	- 18.4	20.1	- 2.4	.5	- 1.9	- 17.4	14.7	2.2
.5	- 4.4	- 18.4	20.0	- 2.8	25.0	- 1.7	- 17.3	14.5	2.1
.6	- 4.4	- 18.3	19.9	- 3.3	.5	- 1.5	- 17.3	14.2	1.7
.7	- 4.3	- 18.3	19.7	- 3.7	26.0	- 1.4	- 17.3	14.0	1.3
.8	- 4.3	- 18.3	19.6	- 4.1	.5	- 1.3	- 17.3	13.9	1.0
.9	- 4.2	- 18.2	19.4	- 4.4	27.0	- 1.1	- 17.4	13.8	0.9
19.0	- 4.2	- 18.2	19.2	- 4.6	.5	- 0.9	- 17.5	13.8	1.0
.1	- 4.2	- 18.2	19.1	- 4.8	28.0	- 0.7	- 17.8	13.8	1.0
.2	- 4.2	- 18.1	19.0	- 5.0	.5	- 0.6	- 18.1	14.0	1.3
.3	- 4.1	- 18.1	18.8	- 5.2	29.0	- 0.4	- 18.5	14.2	1.7
.4	- 4.1	- 18.0	18.7	- 5.3	.5	- 0.2	- 18.8	14.6	2.1
.5	- 4.1	- 18.0	18.6	- 5.3	30.0	0.0	- 19.2	15.0	2.8
.6	- 4.1	- 18.0	18.5	- 5.2	.5	0.2	- 19.6	15.5	3.5
.7	- 4.0	- 18.0	18.4	- 5.1	31.0	0.3	- 19.9	15.9	4.2
.8	- 4.0	- 17.9	18.3	- 5.0	.5	0.4	- 20.2	16.1	5.0

TABLE III-C (continued)

$$T_n - T_{CCT-64} \text{ in mK}$$

T_n \ n	NBS-1955	PSU	PRMI	NPL	T_n \ n	NBS-1955	PSU	PRMI	NPL
32.0	0.3	- 20.5	16.4	5.8	48.5	- 3.3	- 13.4	16.4	14.2
.5	0.2	- 20.8	16.6	6.6	49.0	- 3.0	- 13.0	16.2	14.5
33.0	- 0.1	- 21.0	16.7	7.3	.5	- 2.7	- 12.5	15.9	14.7
.5	- 0.5	- 21.1	16.8	8.0	50.0	- 2.5	- 12.1	15.6	14.9
34.0	- 1.0	- 21.2	16.7	8.5	.5	- 2.3	- 11.8	15.2	15.0
.5	- 1.7	- 21.2	16.6	9.0	51.0	- 2.1	- 11.6	14.8	15.0
35.0	- 2.4	- 21.2	16.5	9.3	.5	- 1.9	- 11.4	14.4	14.9
.5	- 3.1	- 21.2	16.3	9.6	52.0	- 1.6	- 11.3	14.0	14.7
36.0	- 3.8	- 21.1	16.1	9.8	.5	- 1.2	- 11.2	13.6	14.4
.5	- 4.5	- 21.0	15.9	9.8	53.0	- 0.7	- 11.2	13.3	14.1
37.0	- 5.1	- 21.0	15.9	9.8	.5	- 0.2	- 11.3	13.0	13.6
.5	- 5.6	- 20.9	15.8	9.8	54.0	0.4	- 11.4	12.6	13.1
38.0	- 6.1	- 20.8	15.8	9.8	.5	1.0	- 11.6	12.3	12.5
.5	- 6.5	- 20.7	15.6	9.7	55.0	1.6	- 11.7	12.1	11.7
39.0	- 6.8	- 20.5	15.6	9.6	.5	2.3	- 11.8	11.9	10.8
.5	- 7.0	- 20.3	15.7	9.5	56.0	2.9	- 11.9	11.8	9.9
40.0	- 7.2	- 20.1	15.7	9.3	.5	3.6	- 11.9	11.8	9.0
.5	- 7.3	- 19.9	15.8	9.3	57.0	4.3	- 12.0	12.0	8.0
41.0	- 7.3	- 19.7	15.9	9.3	.5	4.9	- 11.9	12.2	7.0
.5	- 7.2	- 19.4	16.0	9.3	58.0	5.6	- 11.9	12.5	6.0
42.0	- 7.0	- 19.1	16.1	9.4	.5	6.2	- 11.8	12.9	5.0
.5	- 6.7	- 18.8	16.3	9.5	59.0	6.7	- 11.7	13.3	4.1
43.0	- 6.4	- 18.4	16.5	9.7	.5	7.2	- 11.6	13.8	3.1
.5	- 6.1	- 18.0	16.7	10.0	60.0	7.5	- 11.4	14.4	2.2
44.0	- 5.8	- 17.6	16.9	10.3	.5	7.7	- 11.2	15.0	1.3
.5	- 5.5	- 17.1	17.0	10.7	61.0	7.8	- 11.1	15.5	0.4
45.0	- 5.2	- 16.6	17.1	11.1	.5	7.9	- 11.1	16.0	- 0.4
.5	- 4.9	- 16.1	17.2	11.5	62.0	7.8	- 11.1	16.6	- 1.2
46.0	- 4.7	- 15.6	17.1	12.0	.5	7.6	- 11.1	17.2	- 1.8
.5	- 4.4	- 15.2	17.1	12.5	63.0	7.3	- 11.2	17.8	- 2.3
47.0	- 4.1	- 14.8	17.0	13.0	.5	7.1	- 11.3	18.3	- 2.7
.5	- 3.8	- 14.3	16.9	13.4	64.0	6.8	- 11.6	18.8	- 3.1
48.0	- 3.5	- 13.9	16.7	13.8	.5	6.5	- 12.0	19.3	- 3.4

TABLE III-C (continued)

$$T_n - T_{CCT-64} \text{ in mK}$$

T_n \ n	NBS-1955	PSU		PRMI	NPL	
65.0	6.1	-	12.6	19.7	-	3.5
.5	5.8	-	13.4	20.0	-	3.4
66.0	5.5	-	14.3	20.3	-	3.4
.5	5.2	-	15.1	20.6	-	3.2
67.0	5.1	-	15.7	20.9	-	2.9
.5	5.0	-	16.0	21.1	-	2.6
68.0	5.0	-	16.1	21.3	-	2.2
.5	5.2	-	16.2	21.4	-	1.6
69.0	5.5	-	16.1	21.5	-	1.0
.5	5.8	-	16.0	21.5	-	0.3
70	6.3	-	15.8	21.6	0.4	
71	7.5	-	15.2	21.8	1.7	
72	9.0	-	14.4	22.0	3.2	
73	10.7	-	13.7	22.2	4.6	
74	12.4	-	12.9	22.5	5.8	
75	14.0	-	12.4	22.8	6.8	

T_n \ n	NBS-1955	PSU		PRMI	NPL
76	15.6	-	12.1	23.1	7.5
77	17.0	-	12.0	23.4	7.9
78	18.2	-	12.2	23.8	8.1
79	19.1	-	12.7	24.3	7.8
80	19.5	-	13.5	24.9	7.2
81	19.5	-	14.4	25.5	6.5
82	19.1	-	15.5	26.1	5.6
83	18.4	-	16.7	26.7	4.7
84	17.3	-	17.9	27.1	3.9
85	15.8	-	19.0	27.4	3.4
86	13.9	-	19.7	27.6	3.2
87	11.7	-	20.2	27.6	3.2
88	9.4	-	20.6	27.5	3.8
89	7.3	-	20.7	27.6	4.6
90	5.6	-	20.5	27.9	5.9
91	4.7	-	19.9	28.4	7.7

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EXPERIMENTS AND RESULTS

1. Low temperature equipment

a. Three slightly different apparatuses were used to measure resistances of platinum thermometers and vapour pressures of different cryogenic liquids at thermal equilibrium. Sketches of the three apparatuses are given in the figures IV-1, IV-2 and IV-3.

In apparatus A (fig.IV-1), which was designed by Van Dijk [69] for the calibration of thermometers, four platinum thermometers were placed in holes in a copper block that was suspended in a can made of German silver. This can was also the reservoir of the vapour pressure thermometer. The level of the liquid in the can had to be below the top of the copperblock to avoid superheating of the surface of the liquid by heat influx from above. The volume of the liquid in the can was usually about 8 cm^3, but the results do not change significantly when the volume is varied between 5 cm^3 and 10 cm^3. The first can was surrounded by a second one, made of brass, in which the gas pressure could be varied. In this way the heat contact between the inner can and the cooling liquid could be adjusted. Over a length of 25 cm the vapour pressure capillary was surrounded by the tube leading from the second can to the top of the cryostat in order to prevent condensation in the capillary. The whole apparatus was placed in a cryostat in which the level of the cooling liquid was always kept below the connection of the vapour pressure capillary to a wider tube which had no jacket. In this apparatus measurements of the triple points of oxygen, nitrogen and hydrogen with a long period of constant temperature were possible because of the large amount of liquid in the vapour pressure thermometer, although the period of constant temperature was shortened by some heat input through the tubes from the top of the cryostat. The replacement of ther-

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mometers in this apparatus was rather difficult and a rather
large amount of pure gas was required to fill the vapour pressure
thermometer.

Fig. IV-1

Apparatus A for measurements
with platinum thermometers and
for vapour pressure measurements
at low temperatures.

Fig. IV-2

Apparatus B for measurements
with platinum thermometers and
for vapour pressure measurements
at low temperatures.

To compare in a simpler way a number of thermometers with a
vapour pressure thermometer without carrying out triple point
measurements apparatus B (fig. IV-2) was constructed in 1964. The
copperblock has the small reservoir of a vapour pressure thermo-
meter in its center. This reservoir is surrounded by holes in
which platinum thermometers can be placed. The copperblock is in

B

R

H2

Th 4
Th 2

A

Cu

brass

Th 1

H1

1 cm

Th 3
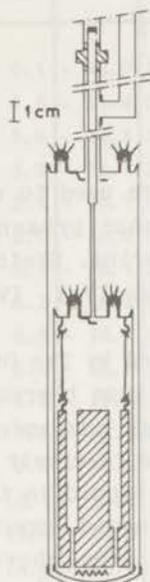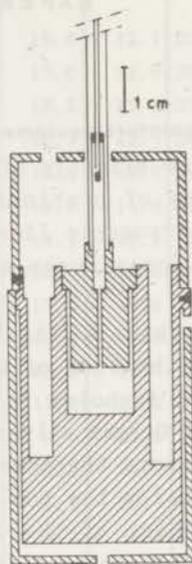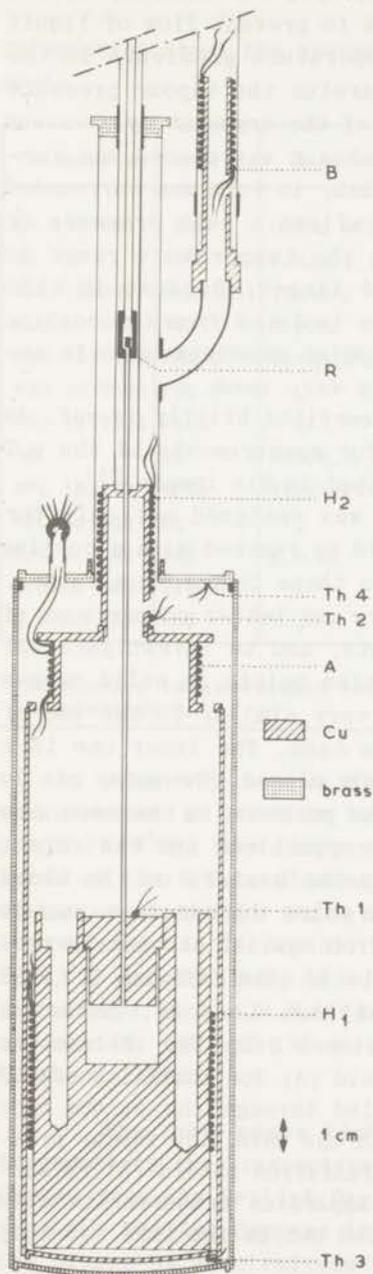
Fig. IV-3

Apparatus C for measurements
with platinum thermometers and
for vapour pressure measurements
at low temperatures.

direct contact with the cooling liquid. Two not entirely closed copper shields are fitted to the block to prevent flow of liquid around the block and to suppress temperature gradients in the liquid around the block. In this apparatus the vapour pressure capillary is surrounded up to the top of the cryostat by a vacuum tube. The glass dewar in which apparatus B was placed was surrounded by a closed metal cylinder which, in turn was surrounded by a second dewar. This arrangement allows a bath pressure of about three atmospheres which makes the temperature range in which measurements can be performed larger. Because in this apparatus the copperblock could not be isolated from the cooling bath, it is not suitable for triple point measurements. In apparatus B eight platinum thermometers were used.

Both apparatus A and B are also described briefly in ref. 49 and ref. 70 and were used by Moussa for measurements of the p, T relation of liquid nitrogen and described in his thesis [71].

In 1964 apparatus C (fig. IV-3) was designed not only for measurements at temperatures that could be reached with a cooling bath but also for measurements between these temperature ranges. This apparatus was constructed to carry out better comparisons of thermometers, to measure triple points, and to investigate the possibility of the use of the transition points in solid oxygen as fixed points. The copperblock is very similar to the one of apparatus B. It is surrounded by two cans. The inner one is a radiation shield which is not completely closed. The outer can is immersed in the cooling liquid. The gas pressure in the cans can be adjusted. The temperature of the copperblock and the shield can be adjusted and kept constant by the heaters on the block (H_1) and on the shield (H_2). Temperature differences can be measured by means of the gold 0.03% iron against chromel thermocouples Th_1 to Th_4 (sensitivity 10 to 15 $\mu V/K$ between 2 K and 100 K, manufactured by Johnson Matthey, London). Before a measurement heater H_1 was always switched off. The thermometer leads are glued to the top of the shield (A) for thermal contact. The wires of the thermocouples are led through the vacuum tube and brought in thermal contact (B) with the bath. The vapour pressure capillary in which there is a radiation shield (R) is surrounded by a vacuum tube. With this apparatus measurements with five platinum thermometers were carried out in the same cryostat as was used for apparatus B.

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TABLE IV-A

Information about the thermometers which are used for the measurements.

Thermometer	Abbrev.	Manufacturer	Calibrated at	$R(0^{\circ}C)$ in Ω	Apparatus
LN 1137601	LN	Leeds & Northrup	N.B.S.	25.5358	A, B, C
T4	T4	P.R.M.I.	P.R.M.I.	25.0349	A, B, C
NPL 153371	NPL1(B1)	Tinsley	N.P.L.	25.3780	A
K.O.L. 143	143	K.O.L.	---	23.8088	A
NBS 1575702	NBS 2	Leeds & Northrup	N.B.S.	25.5597	B
PSU 1577533	PSU 3	" "	P.S.U.	25.5359	B
PSU 1577534	PSU4	" "	P.S.U.	25.5149	B
T2	T2	P.R.M.I.	P.R.M.I.	25.0894	B
NPL 153373	NPL3	Tinsley	N.P.L.	24.9830	B
NPL 164956	B2	"	N.P.L.	24.2724	B
K.O.L. 143*	143	K.O.L.	---	23.8308	C
K.O.L. 145	145	"	---	23.2417	C
K.O.L. 153	153	"	---	25.3304	C

*Thermometer 143 was repared between the measurements in apparatus A and in apparatus C.

b. A survey of the thermometers that were used for the measurements is given in table IV-A. The resistances at the ice point ($R(0^{\circ}C)$) are those which are measured at the K.O.L. in terms of the K.O.L. standard resistance. The changes in the resistances at the ice point in the course of the measurements are less than $2 \times 10^{-4} \Omega$ for all thermometers. The thermometers NBS2, PSU4, T2 and NPL3 were also used for the comparison of the national scales at the N.P.L. and the P.R.M.I. [22,23]. The thermometers 143, 145 and 153 were compared with thermometer LN at the K.O.L. in 1962.

c. The pure gases that were used in the vapour pressure thermometers are, respectively:
Oxygen from the British Oxygen Company in apparatus A and B and from the Philips Company in apparatus C. Both companies prepare the oxygen by electrolysis of air-free water;

20.4 K-equilibrium hydrogen was prepared in the way which is in use at the K.O.L. for several years and which was described recently by Ter Harmsel [72];
Helium was taken from the laboratory stock and led over charcoal at liquid nitrogen temperature before it was condensed in the vapour pressure thermometer.

2. The resistance measurement

In these measurements the potentiometer method is used for the accurate determination of resistances. With a potentiometer the voltage over an unknown resistance carrying a current is compared with the voltage over a standard resistance carrying the same current.
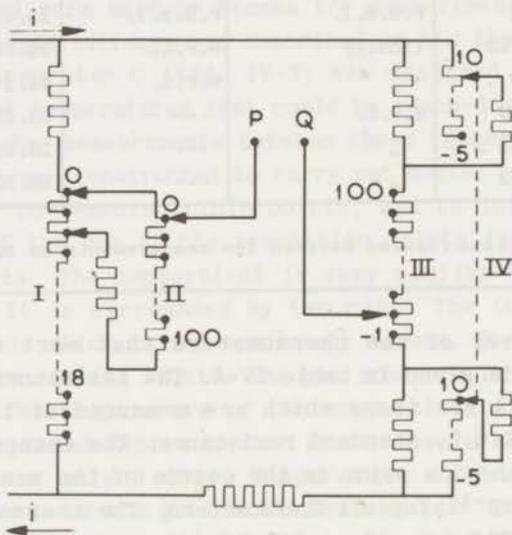
Fig. IV-4

Scheme of the main circuit of the four dial Vernier potentiometer used for the resistance measurements.

The presision potentiometer with which the resistances of the thermometers has been measured is a Vernier potentiometer manu-factured by Tinsley in London in 1950. It is a four dial poten-

tiometer with a first dial consisting of 18 very nearly equal
resistances, a second dial and a third dial consisting of 100
very nearly equal resistances each and a fourth dial consisting
of 16 nearly equal steps. A scheme of the main circuit of the
potentiometer is given in fig. IV-4. The main branch of the
potentiometer contains the dials I and II. The dials III and
IV are in a second branch of the potentiometer. All separate re-
sistances of dial I are compared with each other at several
temperatures with the aid of a Diesselhorst potentiometer and
special contact pins. The resistances of the second dial are in
a shunt over two steps of the first dial. This construction is
called a Vernier shunt. It is the main source of corrections of
the potentiometer because the contacts carry a part of the po-
tentiometer current and the contact resistances are in general
not the same for the different steps and change slightly with
time. Therefore the corrections due to the contact resistances
have to be determined every one or two years. The fourth dial
consists of two resistances with variable shunts in the same
branch of the potentiometer as the third dial.

The resistances are all made of manganin wire. The voltage
over each step of the potentiometer is expressed in terms of the
voltage over the tenth step of the first dial by intercomparisons
of the steps. The accuracy reached with this potentiometer in the
comparison of resistances is estimated to be better than the
equivalent of one step of the last dial. That means that, when
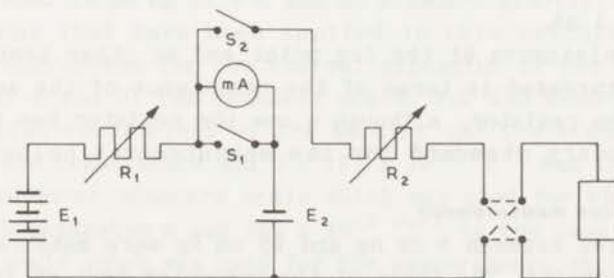
Fig. IV-5

Circuit for the current supply of the potentiometer or of the
resistance thermometers.

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the first dial is on 10 or higher, the accuracy is better than 1 in 10^6. The galvanometer allows a zero setting within 10^{-8}V (1 mm deflection on the scale at a distance of 4 m from the galvanometer corresponds to $2x10^{-8}$V).

The direct currents in the potentiometer circuit and in the platinum thermometer circuit are stabilized using two stabilizing circuits such as shown in fig. IV-5. In these circuits the main current which comes from battery E_1, is adjusted with resistance R_1 and can be measured with the milliammeter when the switches S_1 and S_2 are open. The resistance R_2 must be adjusted in such a way that the battery E_2 of which the voltage is nearly one third of that of battery E_1, gives no current. This can be checked with the milliammeter when S_1 is open and S_2 is closed. During the measurements both switches are closed. If the voltage of E_1 changes, the current in the potentiometer circuit or in the resistance thermometer circuit is kept constant by the battery E_2. All batteries are placed in a thermally insulated box. In the two circuits the currents still can change but the changes will be very slow and continuous.

During the measurements the potentiometer current and the current through the thermometers could be reversed to eliminate effects of thermal voltages in the circuits.

The current in the platinum thermometers was for the measurements at helium temperatures 10 mA, for the measurements at hydrogen temperatures 5 mA and for the measurements at oxygen temperatures 2 mA in apparatus A and apparatus B and usually 1 mA in apparatus C. The ice point resistances were determined with a current of 1 mA.

The resistances at the ice point and at other temperatures were all expressed in terms of the resistance of the same standard ten ohm resistor, although a one ohm resistor has been used as a secondary standard for the measurements below 23.5 K.

3. The pressure measurement

Pressures between 5 cm Hg and 95 cm Hg were measured with a mercury manometer. The tubes of the manometer have an inner diameter of 18 mm. In a tube of this diameter effects of capillary depression are usually negligible. A standard scale is placed beside the manometer. The position of a mercury meniscus could be determined by comparison of the flat top of the meniscus with the

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nearest millimeter divisions on the standard scale by means of the telescope-micrometer of a cathetometer. With this measuring system the distance between two mercury levels may be determined with an accuracy of 0.02 mm. The manometer was placed in an aluminium box in order to diminish the temperature gradients in the mercury. The temperature of the manometer was measured with three mercury thermometers at three levels in the aluminium box. One leg of the manometer was connected to the vapour pressure thermometer, the other to a high vacuum pump.

For pressures above 95 cm Hg the manometer was used with the "vacuum side" open to the atmosphere. The atmospheric pressure was measured with a second manometer system.

Pressures below 5 cm Hg were measured with an oil manometer placed beside the mercury manometer. The thermal expansion coefficient of the Octoil-S in the manometer was determined previously between $18^{\circ}C$ and $27^{\circ}C$. Comparisons of pressure readings with the oil manometer with pressure readings with the mercury manometer showed for the density of the oil no systematic deviations from the density as given by the supplier $(0.9103 \text{ g/cm}^3$ at $25^{\circ}C)$. The accuracy of the determination of the distance between two oil levels is 0.03 mm. Before each set of measurements the oil manometer was pumped to high vacuum for a few hours and heated to about $50^{\circ}C$ to get rid of the gas dissolved in the oil.

Pressures at the surface of the liquid in the vapour pressure thermometer were calculated from the measured level differences and expressed in mm Hg at $0^{\circ}C$ and at standard gravity. The various corrections that have been applied in this calculation are:

a. A correction for the thermal expansion of the mercury or the Octoil-S and of the standard scale. For the mean difference in expansion coefficient of the mercury and the standard scale between room temperature and $0^{\circ}C$ 181×10^{-6} $^{\circ}C^{-1}$ was taken in the case of an invar standard scale which was used for the measurements with apparatus A and 163×10^{-6} $^{\circ}C^{-1}$ in the case of a brass standard scale which was used for the measurements with apparatus B and apparatus C. The level differences measured with the oil manometer were reduced to mm Oil at $20^{\circ}C$ using 7.8×10^{-4} $^{\circ}C^{-1}$ for the thermal expansion coefficient of Octoil-S and were then multiplied by the factor 0.06722 to obtain pressures in mm Hg at $0^{\circ}C$.

b. A correction for the deviation of the local acceleration due to gravity (g_1) from the standard acceleration due to gravity (g_n). Cath [56] used for g_1 the value 981.276 cm/s^2 and this value is in good agreement with the value that may be calculated from the local latitude and altitude with the use of the formula given in ref. 73. With g_1 according to Cath 62×10^{-5} p has to be added to the measured pressure.

c. A correction for the pressure difference due to the difference in weight of the gas columns above the mercury level and above the liquid in the vapour pressure thermometer. This aerostatic head correction is about the equivalent of 1.5 mK for the oxygen vapour pressures and even smaller for the hydrogen vapour pressures. Therefore it can be calculated with sufficient accuracy from an assumed temperature gradient along the vapour pressure capillary.

d. A correction for the thermomolecular pressure difference. This correction is negligible except for the measurements of the pressure at the triple point of oxygen. In this case the pressure at the low temperature side of the vapour pressure capillary is about 0.002 mm Hg lower than the measured pressure.

The total inaccuracy of these corrections is of the same order of magnitude as the inaccuracy of the pressure readings.

4. Procedure of the measurements

A description of the procedure of the measurements with apparatus C includes also the main points of the procedures of the measurements with apparatus A and apparatus B.

Pure gas was condensed in the vapour pressure thermometer at the beginning of each set of measurements while the outer can contained some gas for heat exchange.

For measurements at temperatures that could be reached with the cooling bath the exchange gas was left in the outer can. To cool the heavy copper block mainly by gas conduction required a rather long time. The measurements were usually started at the lowest temperature after which the temperature of the apparatus could be adjusted at a higher value in a reasonable time using the heaters H_1 and H_2. During a measurement the temperature of the bath was adjusted as good as possible to the temperature of the block and maintained at that temperature by means of a mano-

stat or, for pressures below 5 cm Hg, by hand. A heater in the bath served to establish and to maintain the normal hydrostatic temperature gradient. In oxygen below 60 K, however, the normal hydrostatic temperature gradient is very large because of the very small value of dp/dT and this is probably the reason why it was nearly impossible to obtain reproducible measurements of the vapour pressure of oxygen below 60 K. The shield was also brought to the same temperature as the block. To come sufficiently close to a complete temperature equilibrium was then a matter of time. The measurements were started when the temperature drift was smaller than 1 mK per minute during ten minutes. One complete measurement consisted of the comparison of each thermometer with one chosen standard thermometer and of measurements of the vapour pressures during the complete series of thermometer comparisons lasting for at least half an hour.

For measurements in which the temperature of the bath had to be different from the temperature of the block and for triple point measurements the outer can was evacuated to a pressure lower than 10^{-4} mm Hg. For the triple point measurements the temperature of the block was brought below the triple point before the evacuation of the outer can. Then the temperature of the bath was raised a little above the triple point and the temperature change of the block was observed by measuring the thermometer resistance. The pressure was determined when the temperature was constant during the passage of the triple point. For the measurements at the transition points in solid oxygen the vapour pressure thermometer was filled at liquid nitrogen temperature. After this the nitrogen was boiled out of the cryostat which was then filled with liquid hydrogen. At 20 K some helium gas was admitted to the vapour pressure thermometer for heat contact between the solid oxygen and the copper block. The temperature of the block was adjusted some hundredths kelvin below the transition temperature and the temperature of the shield a few tenths kelvin above the transition temperature and then the temperature change of the block was observed by measuring the thermometer resistance while the temperature of the shield was kept constant as good as possible.

5. Data obtained from the experiments

The direct results of the measurements (the corrected vapour

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pressures, the corresponding W values for the standard thermo-
meter and the differences between the W values of the standard
thermometer and the W values of the other thermometers) are
presented in the tables IV-B to IV-D. To indicate in these tables
the temperatures at which the measurements were performed the
temperatures that can be calculated from the vapour pressure
measurements are given.

These temperatures were derived from the T_{58} scale for the
helium measurements, from the T_{L60} scale [74,75]*, which has been
used in Leiden for several years, for the hydrogen measurements
and from the p,T relation which is derived in chapter II for the
oxygen measurements. All measurements got a number to which will
be referred in the following chapters.

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* The relation between the vapour pressure of $e-H_2$ and T_{L60} is:
  $$^{10}\log p = 4.635384 - \frac{44.2674}{T} + 0.021669\ T - 0.000021\ T^2,$$ where p
  is expressed in mm Hg at $0°C$ and T is the numerical value of the
  temperature expressed in kelvins.

TABLE IV-B

Resistance ratios W for platinum thermometers and vapour pressures p measured in apparatus A.

No.	Date	Pressure mm Hg at $0°C$	W_{LN} $\times 10^{-6}$	$W_{LN}-W_{T4}$ $\times 10^{-6}$	$W_{LN}-W_{143}$ $\times 10^{-6}$	$W_{LN}-W_{NPL1}$ $\times 10^{-6}$	T_p K
		Helium temperatures					T_{58}
1	13-6-'63	4.093	640.66	283.79	96.88	132.09	1.527
2	"	36.28	644.16	283.90	97.10	132.13	2.156
3	"	117.95	648.27	283.51	96.85	131.74	2.729
4	"	361.88	655.40	282.20	96.48	131.01	3.514
5	"	773.66	664.77	281.45	96.34	130.48	4.234
6	17-3-'64	2.517	639.46	283.07	95.99	---	1.429
7	"	15.838	641.73	283.04	96.25	---	1.870
8	"	34.65	643.29	282.97	96.22	---	2.137
9	"	100.49	646.75	282.69	96.15	---	2.638
10	"	213.74	650.74	282.07	96.12	---	3.110
11	"	402.05	655.78	281.54	96.12	---	3.603
12	"	772.73	663.73	280.73	95.52	---	4.233
		Hydrogen temperatures					T_{L60}
13	28-5-'63	67.05	1651.8	293.9	104.5	130.3	14.2207
14	"	247.75	2655.2	295.1	109.0	132.3	17.0017
15	"	795.83	4736.0	290.5	115.7	132.8	20.4165
16	29-5-63	63.69	1626.6	293.2	104.5	130.5	14.1281
17	"	103.24	1894.5	294.6	106.2	131.3	15.0429
18	"	160.88	2225.0	295.3	107.6	132.1	15.9820
19	"	789.77	4718.4	290.7	115.3	132.7	20.3904
20	"	248.58	2659.7	295.4	109.5	132.7	17.0100
21	"	518.12	3766.5	293.2	113.2	133.0	19.0333
22	7-6-'63	647.18	4230.6	291.4	113.4	132.1	19.7296
23	"	411.68	3355.4	293.5	111.2	132.2	18.3567
24	"	313.97	2951.5	294.6	109.8	132.1	17.6112
25	"	200.50	2428.8	294.9	108.1	132.4	16.4879
26	"	129.92	2054.6	295.0	106.6	131.5	15.5166
27	"	77.38	1725.0	294.0	105.0	130.8	14.4843
28	10-6-'63	---	1366.5	291.5	102.2	129.4	---

TABLE IV-B (continued)

No.	Date	Pressure mm Hg at $0°C$	W_{LN} $\times 10^{-6}$	$W_{LN}-W_{T4}$ $\times 10^{-6}$	$W_{LN}-W_{143}$ $\times 10^{-6}$	$W_{LN}-W_{NPL1}$ $\times 10^{-6}$	T_p K
		Hydrogen temperatures (continued)					T_{L60}
29	10-6-'63	---	1185.5	288.0	100.5	128.0	---
30	"	---	1030.8	285.0	99.1	127.2	---
31	"	---	909.6	281.8	97.3	126.1	---
32	11-6-'63	52.73	1541.4	293.0	103.5	130.1	13.7977
33	12-6-'63	---	853.5	280.0	95.8	126.5	---
34	"	63.71	1626.3	293.3	104.5	130.1	14.1287
35	"	794.18	4730.2	289.8	115.5	132.1	20.4094
		Oxygen temperatures					T_{pc}
36	28-8-'63	18.475	136501.5	251.3	135.2	131.1	65.2498
37	29-8-'63	48.008	157156.5	245.8	132.6	126.2	70.1184
38	"	225.37	199658.4	235.2	128.3	127.1	79.9769
39	"	431.13	221846.1	231.1	130.2	124.9	85.0926
40	"	780.67	245064.2	234.3	132.9	131.0	90.4454
41	2-9-'63	774.03	244716.7	236.1	136.5	137.0	90.3638
42	"	771.47	244565.3	229.0	129.6	---	90.3315
43	14-9-'63	1.097	92099.7	263.3	137.3	135.3	54.3597
44	24-9-'63	1.098	92086.8	255.4	135.3	130.3	54.3626
45	15-10-'63	178.08	192316.6	239.6	131.5	128.3	78.2820
46	"	345.13	213894.7	234.5	136.4	134.1	83.2589
47	"	620.98	235757.6	234.2	134.0	129.6	88.2981
48	16-10-'63	13.809	130873.1	250.3	132.5	128.0	63.9094
49	"	85.52	171557.5	239.4	134.8	127.3	73.4721
50	29-1-'64	234.54	200952.6	238.8	140.3	---	80.2718
51	"	296.50	208681.2	243.9	137.0	---	82.0560
52	"	476.83	225582.5	242.3	140.9	---	85.9522
53	"	599.79	234388.8	242.7	138.5	---	87.9820
54	"	748.67	243334.4	241.6	138.3	---	90.0445
55	30-1-'64	768.28	244399.4	227.1	127.3	---	90.2916
56	"	665.01	238498.4	238.8	138.2	---	88.9293
57	24-3-'64	11.550	127568.9	258.5	---	---	63.1165
58	25-3-'64	768.96	244450.0	237.3	---	---	90.3001

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Resistance ratios W for platinum thermometers and vapour pressures p measured in apparatus B.

No.	Date	Pressure mm Hg at 0 C	W_{T4} $\times 10^{-6}$	$W_{PSU4}-W_{T4}$ $\times 10^{-6}$	$W_{NBS2}-W_{T4}$ $\times 10^{-6}$	$W_{B2}-W_{T4}$ $\times 10^{-6}$	$W_{PSU3}-W_{T4}$ $\times 10^{-6}$	$W_{T2}-W_{T4}$ $\times 10^{-6}$	$W_{LN}-W_{T4}$ $\times 10^{-6}$	$W_{NPL3}-W_{T4}$ $\times 10^{-6}$	T_p K
		Helium temperatures									T_{58}
59	23-6-'64	766.56	384.3	346.8	332.9	141.3	343.6	+0.2	280.5	126.6	4.2241
60	"	1.267	357.3	349.9	336.0	141.2	346.7	+0.2	283.1	127.4	1.3082
61	"	5.382	358.5	349.8	336.0	141.5	346.6	+0.1	283.2	127.4	1.5872
62	"	31.139	361.4	349.6	335.7	141.4	346.3	+0.1	283.1	127.3	2.0966
63	"	134.39	367.0	348.8	335.0	141.4	345.5	+0.1	282.4	126.9	2.8065
64	24-6-'64	359.58	374.4	347.9	334.1	141.4	344.7	+0.1	281.8	126.9	3.5087
65	"	766.20	384.3	346.8	333.0	141.2	343.5	+0.3	280.7	126.5	4.2237
66	"	1168.94	392.5	346.0	332.0	141.2	342.8	+0.3	279.9	126.4	4.7048
67	"	1585.58	400.0	345.5	331.5	141.2	342.2	+0.5	279.3	126.2	5.0918
		Hydrogen temperatures									T_{L60}
68	17-6-'64	70.05	1380.8	367.8	349.8	155.4	364.7	+1.4	290.9	131.9	14.3003
69	"	135.01	1789.0	370.3	351.9	158.4	367.9	+1.0	291.9	130.9	15.5986
70	"	378.39	2928.6	373.7	350.8	156.8	371.0	+1.0	290.1	124.3	18.1189
71	"	523.03	3491.7	374.4	348.8	155.3	370.5	+1.1	291.6	121.6	19.0620
72	"	779.10	4391.6	372.6	345.5	154.1	369.1	+1.1	286.8	116.8	20.3441
73	18-6-'64	47.89	1215.0	367.2	349.6	155.2	362.9	+1.8	291.7	133.8	---
74	"	10.809	846.0	359.0	342.8	150.4	356.1	+0.9	285.1	133.5	---
75	"	---	690.1	351.8	337.0	145.0	348.6	+1.2	281.1	130.6	---
76	"	---	541.8	347.0	332.2	142.5	343.0	+0.5	278.4	128.6	---

TABLE IV-C

TABLE IV-C (continued)

No.	Date	Pressure mm Hg at 0°C	W_{T4} x10^{-6}	$W_{PSU4}-W_{T4}$ x10^{-6}	$W_{NBS2}-W_{T4}$ x10^{-6}	$W_{B2}-W_{T4}$ x10^{-6}	$W_{PSU3}-W_{T4}$ x10^{-6}	$W_{T2}-W_{T4}$ x10^{-6}	$W_{LN}-W_{T4}$ x10^{-6}	$W_{NPL3}-W_{T4}$ x10^{-6}	T_p K
		Hydrogen temperatures (continued)									T_{L60}
77	19-6-'64	235.92	2307.0	373.5	352.4	157.9	370.1	+1.1	292.1	128.5	16.8804
78	"	774.09	4374.7	---	345.2	154.2	---	---	---	117.0	20.3221
79	"	1237.72	5825.6	371.5	341.3	152.2	366.7	+2.5	286.9	112.5	22.0253
80	"	1586.50	6823.0	368.9	337.1	149.7	365.9	+1.0	280.2	107.7	23.0235
81	"	1027.22	5189.3	372.1	342.4	152.6	369.0	+0.6	284.2	113.5	21.3215
		Oxygen temperatures									T_{pc}
82	12-5-'64	51.97	158808	328	259	115	335	-3	230	67	70.5602
83	13-5-'64	771.40	244339	306	236	107	307	+4	220	60	90.3307
84	"	771.65	244348	---	---	---	---	---	220	--	90.3340
85	14-5-'64	541.96	230198	308	230	106	312	+7	218	59	87.0725
86	"	344.99	213631	315	243	107	312	-5	226	63	83.2558
87	"	233.16	200500	318	244	114	324	+3	228	66	80.2290
88	"	117.50	179925	323	250	122	320	-2	228	57	75.4745
89	26-5-'64	9.245	123332	---	266	119	---	---	---	74	62.1578
90	"	5.371	114217	347	265	124	342	0	250	70	59.9466
91	28-5-'64	771.19	244318	303	227	106	306	+1	211	61	90.3281
92	"	928.52	252229	---	225	115	---	---	---	64	92.1495
93	"	1123.63	260702	273	222	94	301	-5	218	49	94.1041
94	29-5-'64	1356.78	269446	---	221	105	---	---	---	69	96.1252
95	"	---	276211	295	217	101	297	+1	208	57	---

Resistance ratios W for platinum thermometers and vapour pressures p measured in apparatus C.

No.	Date	pressure mm Hg at 0°C	W_{T4} $\times 10^{-6}$	$W_{LN}-W_{T4}$ $\times 10^{-6}$	$W_{145}-W_{T4}$ $\times 10^{-6}$	$W_{143}-W_{T4}$ $\times 10^{-6}$	$W_{153}-W_{T4}$ $\times 10^{-6}$	T_p K	Remarks
	Helium temperatures							T_{58}	
96	28-6-'66	9.62	363.3	276.9	168.5	228.9	141.5	1.729	
97	"	105.61	369.7	276.6	168.1	228.6	141.1	2.666	
98	"	362.20	378.4	275.7	167.6	227.9	140.5	3.514	
99	"	753.77	388.0	274.7	167.2	227.3	139.8	4.206	
	Hydrogen temperatures							T_{L60}	
100	8-6-'66	803.48	4482.5	281.0	160.4	230.3	141.0	20.4493	
101	"	801.99	4477.8	281.2	159.7	230.2	141.0	20.4429	4mA
102	"	246.13	2361.1	286.6	169.7	236.7	143.8	16.9853	
103	"	363.89	2876.9	285.9	167.2	235.2	143.1	18.0105	
104	15-6-'66	71.77	1398.0	285.7	172.9	236.8	143.7	14.3448	
105	"	116.40	1686.4	286.5	172.1	237.7	144.0	15.2869	
106	16-6-'66	52.75	1255.3	285.3	173.0	236.1	143.4	13.7984	tr. point
107	17-6-'66	781.97	4408.9	281.8	159.9	230.5	140.6	20.3566	jacket vac.
108	"	1295.63	6008.6	277.4	153.0	225.7	138.7	22.2038	"
109	"	1586.27	6830.5	275.1	151.0	222.8	137.5	23.0228	"
	Oxygen temperatures							T_{pc}	
110	28-4-'66	799.56	245814	226	88	167	111	90.6760	2mA, gas
111	29-4-'66	804.61	246094	218	91	161	112	90.7370	1mA, vac.

TABLE IV-D

TABLE IV-D (continued)

No.	Date	pressure mm Hg at 0°C	W_{T4} x10^{-6}	W_{LN}-W_{T4} x10^{-6}	W_{145}-W_{T4} x10^{-6}	W_{143}-W_{T4} x10^{-6}	W_{153}-W_{T4} x10^{-6}	T_p K	Remarks
				Oxygen temperatures (continued)				T_{pc}	
112	7-12-'66	163.51	189506	243	94	168	119	77.6868	2mA, gas
113	"	163.56	189520	243	94	167	119	77.6889	2mA, vac.
114	8-12-'66	159.90	188835	230	95	169	121	77.5326	1mA, gas
115	"	159.87	188833	232	95	170	121	77.5313	1mA, vac.
116	26-1-'67	764.70	243963	220	94	157	114	90.2469	1mA, gas
117	13-3-'67	---	91839.5	---	107	183	133	---	tr.p., O_2
118	19-5-'67	1.101	91840.4	---	112	187	133	54.3710	tr.p., O_2
119	"	---	131690	---	100	178	126	---	
120	24-5-'67	---	91850.4	---	108.9	185.2	129.6	---	tr.p., O_2
121	25-5-'67	754.14	243391	221	92	161	113	90.1158	1mA, gas
122	13-6-'67	---	91855.1	---	107.2	---	---	---	tr.p., H_2
			Transition points in solid oxygen						
123	4-3-'67	---	7730.6	---	150.6	---	---	---	H_2 20.4 K
124	8-3-'67	---	7736.4	---	150.4	---	---	---	H_2 23.5 K
125	9-3-'67	---	53507.5	---	113	194	135	---	H_2 20.4 K
126	7-6-'67	---	7726.3	274.2	148.6	221.7	137.6	---	H_2 23.5 K
127	8-6-'67	---	53518.5	254.6	113.7	194.1	135.9	---	H_2 20.4 K
128	13-6-'67	---	53530.0	---	113.0	---	---	---	H_2 20.4 K

CHAPTER V

THE COMPARISON OF TEMPERATURES ON THE CCT–64 SCALE WITH TEMPERATURES DEDUCED FROM p,T RELATIONS. THE REALIZATION OF FIXED POINTS

1. The reproducibility of the platinum thermometers

The accuracy of the results of measurements with calibrated thermometers depends considerably on the reproducibility of these thermometers. In this section therefore attention is paid to this point.

For the thermometers that were used in more than one apparatus the different determinations of the resistances at liquid helium temperatures can give the best information on the reproducibility because at these low temperatures dR/dT is so small that errors introduced by uncertainties in the temperature of the thermometers are smaller than any significant change in the residual resistance ratio $W_0 (= R(0K)/R(0°C))$ of a resistance thermometer itself. For the thermometers LN and T4, which were used in all experiments, the results of the measurements at the lowest temperatures are shown in fig. V-1 and fig. V-2. The changes in the resistance ratios of these thermometers were not negligible but, since changes of the resistance ratios of thermometers are, in first approximation, not temperature dependent, corrections could be applied for these changes. In this way the results obtained with different apparatuses could be compared with improved accuracy.

The reproducibility of the thermometers which were used for the comparison of the national scales was checked by comparing the differences between the W values of different thermometers, which were obtained at temperatures in the liquid hydrogen range at the N.P.L., at the P.R.M.I. and in our experiments. It can be seen from fig. V-3 to fig. V-5 that only the thermometer T2 changed considerably after the measurements at the P.R.M.I. From these figures one may also get an impression of the precision of

the scale comparisons in this temperature range. The scattering of the points is of the order of magnitude of 1×10^{-6} in ΔW and this is the equivalent of 1 mK at 23 K and 4 mK at 14 K.
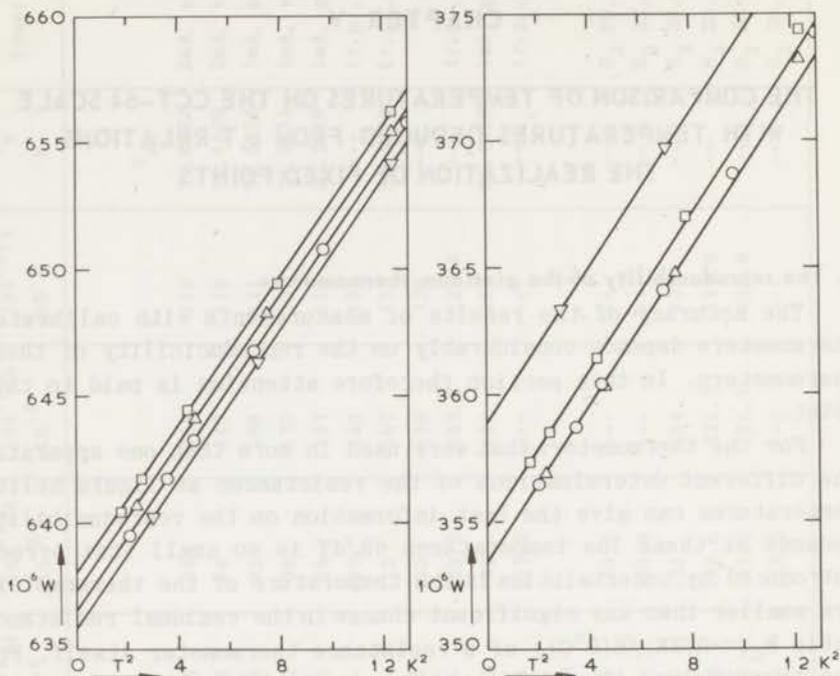

Fig. V-1: Thermometer LN   Fig. V-2: Thermometer T4

W values at liquid helium temperatures as obtained in different series of measurements showing the change of the residual resistance between different series.

The resistances of the thermometers 143, 145 and 153 at liquid helium temperatures were previously determined in 1962. The differences between the resistance ratios obtained in 1962 and those obtained with apparatus A for the thermometer 143 and with apparatus C for the thermometers 145 and 153 are smaller than 1×10^{-6}.

A conclusion that can be drawn from these data is that the reproducibility of platinum thermometers over a period of several

years is in general within 1×10^{-6} in W. However, there are exceptions which require the checking of the constancy of a thermometer from time to time.
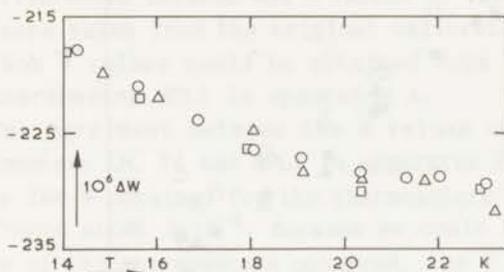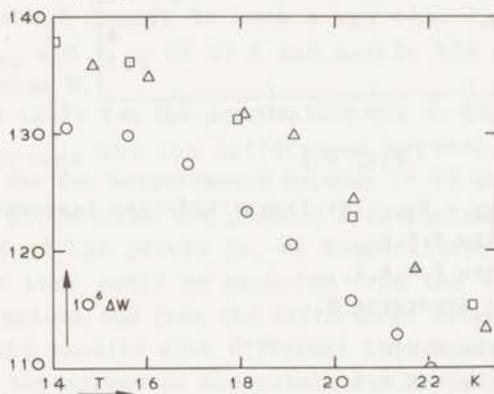
FIG. V-3

$W_{NBS2} - W_{NPL3}$ at liquid hydrogen temperatures.

x measured at the N.P.L.

x measured at the P.R.M.I.

x measured with apparatus B.

FIG. V-4

$W_{NPL3} - W_{T2}$ at liquid hydrogen temperatures.

x measured at the N.P.L.

x measured at the P.R.M.I.
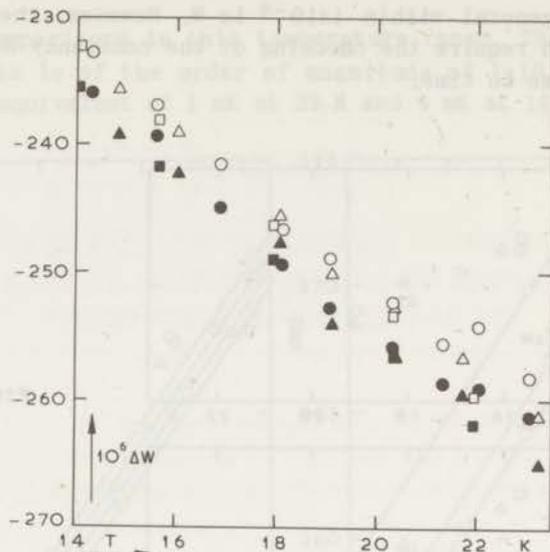
x measured with apparatus B.

FIG. V-5

$W_{PSU3} - W_{NPL3}$ and $W_{PSU4} - W_{NPL3}$ at liquid hydrogen temperatures.

PSU3: □ measured at the N.P.L.

△ measured at the P.R.M.I.

○ measured with apparatus B

PSU4: ■ measured at the N.P.L.

▲ measured at the P.R.M.I.

● measured with apparatus B.

2. The measurements with the hydrogen vapour pressure thermometer

a. Comparison of T_{CCT-64} with T_{L60}*.

From the measured W values of the thermometers NBS2, PSU3, PSU4 and NPL3 in apparatus B values for $\overline{W}$ were obtained using the results for $W-\overline{W}$ from the scale comparisons at the N.P.L. and the P.R.M.I. The results for the thermometer T2, which changed considerably (see section V-1), were omitted. The differences between $\overline{W}$ and the W values for the thermometers LN and T4 obtained in apparatus B were used as calibration data for these thermometers.

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* A provisional analysis of the measurements in apparatus A and apparatus B was given earlier [76].

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Corrections were applied for the changes of the resistances at liquid helium temperatures and the W-$\overline{W}$ data obtained for apparatus B were used to obtain the $\overline{W}$ values for the measurements with the thermometers LN and T4 in apparatus A and apparatus C. The differences between the W values of the thermometers NPL1 and NPL3 were taken from the original calibration data of the N.P.L. and thus $\overline{W}$ values could be obtained from the measurements with the thermometer NPL1 in apparatus A.

The agreement between the $\overline{W}$ values obtained for the three thermometers LN, T4 and NPL1 in apparatus A was satisfactory. The values for $\overline{W}$ obtained for the thermometers LN and T4 in apparatus C differed about 2×10^{-6}. Because we could not determine when the change of the thermometers occurred, the $\overline{W}$ values were changed by a constant amount in such a way that the difference between T_{CCT-64} and T_{L60} at 17 K was nearly the same as obtained with apparatus B.

In table V-A the mean values for $\overline{W}$, the corresponding values for T_{CCT-64} and the differences between T_{CCT-64} and T_{L60} are given for our measurements between 13.8 K and 23 K and in fig. V-6 these differences are plotted as a function of temperature. The spread of the points is, at temperatures above 17 K, a little larger than could be expected from the reproducibility of the thermometers and from the differences between $\overline{W}$ values calculated from the results with different thermometers. At these temperatures the spread of the points may be due to errors in the temperature measurements with the vapour pressure thermometer. In fig. V-6 the differences between T_{CCT-64} and T_{L60} according to the measurements of Hoge and Arnold [77] and according to those of Barber and Miss Horsford [78] are also plotted. The temperatures, which were measured by these authors on the NBS-1939 scale and the NPL scale respectively, were recalculated to the CCT-64 scale by using the differences between the CCT-64 scale and the national scales (see section III-3).

The curve in fig. V-6 gives a smoothed average of the differences between the CCT-64 scale and the L60 scale. For nearly all points the deviations from this curve are smaller than 4 mK and the average deviation from the curve is about 2 mK.

b. The boiling point of e-hydrogen.

The differences in the realizations of the normal boiling

TABLE V-A

$\overline{W}$ and T_{CCT-64} for the measurements between 13,8 K and 23 K.
$\Delta T = T_{CCT-64} - T_{L60}$.

| No.	$\overline{W}$ x10^{-6}	T_{CCT-64} K	ΔT mK	No.	$\overline{W}$ x10^{-6}	T_{CCT-64} K	ΔT mK
	Apparatus A						
13	1520.9	14.2461	25.4	22	4097.7	19.7440	14.4
14	2523.0	17.0168	15.1	23	3222.8	18.3712	14.5
15	4602.4	20.4295	13.0	24	2819.0	17.6263	15.1
16	1496.0	14.1534	25.3	25	2296.8	16.5044	16.5
17	1763.3	15.0648	21.9	26	1922.9	15.5381	21.5
18	2093.0	15.9992	17.2	27	1594.0	14.5081	23.8
19	4585.1	20.4070	16.6	32	1411.1	13.8223	24.6
20	2527.1	17.0257	15.7	34	1495.6	14.1518	23.1
21	3632.9	19.0491	15.8	35	4597.1	20.4186	9.2
	Apparatus B						
68	1542.4	14.3247	24.4	77	2468.6	16.8977	17.3
69	1950.9	15.6168	18.2	78	4530.1	20.3351	13.0
70	3088.4	18.1328	13.9	79	5978.4	22.0388	13.5
71	3650.1	19.0761	14.1	80	6972.9	23.0365	13.0
72	4547.2	20.3575	13.4	81	5343.1	21.3353	13.8
	Apparatus C						
100	4631.9	20.4677	18.4	105	1842.3	15.3046	17.7
101	4627.3	20.4617	18.8	106	1410.9	13.8214	23.0
102	2516.5	17.0027	17.4	107	4558.7	20.3726	16.0
103	3031.1	18.0285	18.0	108	6154.5	22.2238	20.0
104	1553.6	14.3651	20.3	109	6974.6	23.0382	15.4
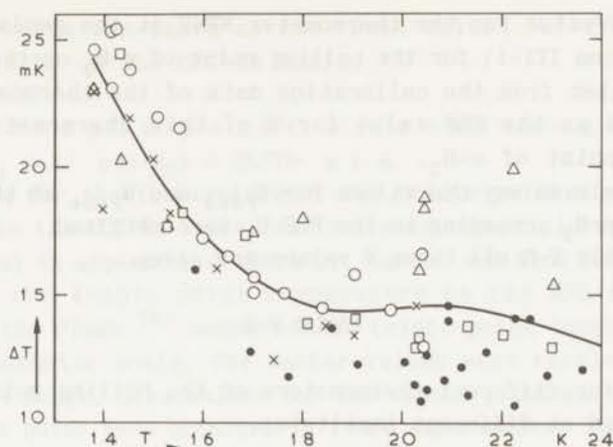
FIG. V-6

Differences between temperatures on the CCT-64 scale deduced from measurements with platinum thermometers and temperatures on the T_{L60} scale deduced from measured vapour pressures of liquid e-H_2 as obtained from our measurements and from measurements of other authors. $\Delta T = T_{CCT-64} - T_{L60}$.

O measured with apparatus A

□ measured with apparatus B

△ measured with apparatus C

• measured by Hoge and Arnold [77]

× measured by Barber and Miss Horsford [78].

point of hydrogen at different institutes can be deduced from W values at this point given for a same thermometer by the different institutes.

The temperature at which the boiling point of 20.4 K-equilibrium hydrogen was realized at the K.O.L. for the thermometers NBS2, PSU3, PSU4 and NPL3 in apparatus B can be deduced from measured W values.

Barber [22] gave a value for W_{NPL3} at the boiling point of e-H_2 and measured the differences between the W values of this thermometer and the thermometers NBS2, PSU3 and PSU4.

For the same thermometers the values of W at the boiling point of normal hydrogen, which is 117 mK higher than that of e-hydrogen, are given by Astrov et al. [23]. These values were recalculated to the boiling of e-H_2.

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The W value for the thermometer NBS2 at the declared value (see section III-1) for the boiling point of e-H_2 on the NBS-1955 scale, taken from the calibration data of the thermometer, has been used as the NBS value for W of this thermometer at the boiling point of e-H_2.

In the same way the values for W_{PSU3} and W_{PSU4} at the boiling point of e-H_2 according to the P.S.U. were obtained.

In table V-B all these W values are given.

TABLE V-B

W values for different thermometers at the boiling point of e-H_2 as obtained at different institutes.

	$10^6 W_{NBS2}$	$10^6 W_{PSU3}$	$10^6 W_{PSU4}$	$10^6 W_{NPL3}$	Remarks
K.O.L.	4673.1	4697.1	4700.6	4444.7	2 measurements
N.P.L.	4675.2	4698.5	4701.5	4445.1	ref. 22
P.R.M.I.	4663.7	4687.5	4691.0	4434.8	ref. 23
N.B.S.	4670.3	---	---	---	declared value
P.S.U.	---	4690.6	4693.7	---	declared value

From the average differences between the W values, obtained at different institutes, it follows that our realization with apparatus B is:

1.6 mK lower than the realization at the N.P.L.,
12.7 mK higher than the realization at the P.R.M.I.,
3.7 mK higher than the realization at the N.B.S. and
8.9 mK higher than the realization at the P.S.U.

Because the average value of our realizations of the boiling point in the three apparatuses is between 1 and 2 mK higher than the realization in apparatus B, the agreement of the realizations at the K.O.L. and at the N.P.L. is satisfactory. The large deviation of the realization at the P.R.M.I. might be due to the fact that the hydrogen of which the boiling point was measured did not have entirely the normal ortho-para composition.

The value of T_{CCT-64} at the boiling point of e-H_2 according to the realizations at the K.O.L. and at the N.P.L. is 20.275 K

and this value was taken as the "best value" for the boiling point of e-H_2 on the CCT-64 scale.

c. The triple point of e-hydrogen and T_{CCT-64} at p(e-H_2) = 25/76 atm.

Values for the temperature of the triple point of e-H_2 were obtained on the CCT-64 scale from our measurements in apparatus A (No. 32) and in apparatus C (No. 106). Barber and Miss Horsford [78] measured the triple point temperature on the NPL scale and Cataland and Plumb [79] measured the triple point temperature on the NBS-acoustic scale. The latter values were recalculated to the CCT-64 scale. Also values for the vapour pressure of e-H_2 at the triple point were obtained in these experiments. Temperatures and vapour pressures at the triple point of e-H_2 are given in table V-C.

TABLE V-C

Temperatures and vapour pressures at the triple point of e-H_2 as obtained by different authors.

	T_{CCT-64} (K)	p(mm Hg)	Remarks
Barber and Horsford [76]	13.828	52.95	T_{NPL} = 13.816 K
Cataland and Plumb [77]	13.825	52.64	$T_{NBS, ac}$ = 13.812 K
This research	13.822	52.74	Table V-A, No. 32 and No. 106

The results of the measurements of the vapour pressure at the triple point of e-H_2 by Ter Harmsel [72], showed a spread of only 0.004 mm Hg. The average value was 52.73 mm Hg at 0°C and at standard gravity. Van Rijn [80] obtained the value 52.74 mm Hg for the vapour pressure of e-H_2 at its triple point. Recently also at the Argonne National Laboratory the value 52.74 mm Hg was obtained [81].

Considering these data T_{CCT-64} = 13.825 K and p = 52.73 mm Hg at 0°C and at standard gravity are recommended as the "best values" for the temperature of the triple point of e-H_2 on the CCT-64 scale and the vapour pressure of e-H_2 at its triple point.

T_{L60} at $p(e-H_2) = 250$ mm Hg is 17.0242 K. The average difference between T_{L60} and T_{CCT-64} at 17.03 K is 15.7 mK (see fig. V-6). Therefore T_{CCT-64} at $p(e-H_2) = 250$ mm Hg is taken equal to 17.0399 K. At this temperature $10^6 \overline{W} = 2533.7$.

d. The temperature on the IPTS-1968 at $p(e-H_2) = 25/76$ a t m.

Using the values 20.280 K and 13.810 K for the temperatures at the boiling point and the triple point of e-H_2 as recommended by the C.C.T. in 1967 and p = 52.73 mm Hg for the vapour pressure of e-H_2 at its triple point, Ter Harmsel [82] calculated the following p,T relation for e-H_2:

$$^{10}\log \frac{p}{p_0} = 1.7411466 - \frac{44.01046}{T} + 0.0235909 \, T - 48.017 \times 10^{-6} \, T^2 \quad (V-1)$$

where p_0 is the pressure at the boiling point and T is the numerical value of the temperature expressed in kelvins.

This p,T relation, calculated at the request of the C.C.T., is based on data obtained:
1. bij Hoge and Arnold [77] from the results of measurements of vapour pressures of e-H_2 at different temperatures measured with a platinum thermometer which was calibrated on the NBS-1939 scale,
2. by Barber and Miss Horsford [78] from the results of measurements in which a platinum thermometer was used which was calibrated on the NPL scale,
3. by Ter Harmsel [72] from calculations in which the results of his measurements of the heat of vaporization of e-H_2 were used,
4. by Van Rijn [83] from the results of measurements with a magnetic thermometer.

Eq. (V-1) is in good agreement with the average of all data if these data are reduced in such a way that the values of p and T at the boiling point and the triple point coincide with the recommended values.

Temperatures calculated by using eq. (V-1) may be denoted $T_{68}(e-H_2)$.

From eq. (V-1) the value 17.0422 K is obtained at $p/p_0 = 25/76$. This temperature is recommended to be used as a fixed point for the IPTS-1968.

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3. The measurements with liquid and solid oxygen

a. C o m p a r i s o n   o f T_{CCT-64} w i t h T_{pc}.

Values of $\overline{W}$ for the measurements with apparatus B and for the measurements with the thermometers LN and T4 with the two other apparatuses in the temperature range of liquid and solid oxygen were obtained in the same way as for the hydrogen measurements. Values of $\overline{W}$ were calculated from the experimental data obtained in apparatus A for the thermometer NPL1 using the results of the comparison of thermometer NPL1 with thermometer B2 by Moussa [71] and the results of the comparison of thermometer B2 with thermometer NPL3 in apparatus B. The values of $\overline{W}$ obtained for the thermometers T4 and NPL1 in apparatus A were in better agreement with each other than with the values of $\overline{W}$ for thermometer LN and therefore the latter values were not used. From the data obtained with apparatus C it can be deduced that the values of $W_{LN} - W_{T4}$ increase considerably with increasing measuring current. In table V-D the values of $\overline{W}$ and the values of T_{CCT-64} are given for the measurements with liquid and solid oxygen; for the measurements with liquid oxygen also $T_{CCT-64} - T_{pc}$ is given (temperatures T_{pc} are deduced from measured vapour pressures, see section II-2e and section IV-5). In fig. V-7 the differences $T_{CCT-64} - T_{pc}$ are plotted versus temperature. The values of $T_{CCT-64} - T_{pc}$ derived from the results of the measurements of Hoge [61] above 80 K are plotted in fig. V-8. The agreement of the points in fig. V-7 with those in fig. V-8 is good.

From the results of our measurements we calculated an expression for the relation between the vapour pressure of liquid oxygen and T_{CCT-64}. This relation is:

$$^{10}\log \frac{p}{p_0} = 9.178515 - \frac{466.40709}{T} - 1.664512 \, ^{10}\log T - 0.01276639 \, T + 49.1062 \times 10^{-6} T^2 \qquad (V-2)$$

where p_0 is the pressure at the normal boiling point and T is the numerical value of the temperature expressed in kelvins. Temperatures according to eq. (V-2) are denoted $T_{CCT-64}(O_2)$.

The p,T relation of oxygen given in eq. (V-2) has its boiling point at 90.1727 K and its triple point at 54.352 K (p = 1.099 mm Hg at 0°C and at standard gravity). The choice of these points is discussed in the next sections.

The differences between $T_{CCT-64}(O_2)$ and T_{pc} are represented by the curves in fig. V-7 and fig. V-8.

TABLE V-D

$\overline{W}$ and T_{CCT-64} for the measurements with liquid and solid oxygen. $\Delta T = T_{CCT-64} - T_{pc}$.

| No.	$\overline{W}$ $\times 10^{-6}$	T_{CCT-64} K	ΔT mK		No.	$\overline{W}$ $\times 10^{-6}$	T_{CCT-64} K	ΔT mK
	Apparatus A							
36	136373	65.2462	- 3.6		48	130747	63.9048	- 4.6
37	157032	70.1157	- 2.7		49	171435	73.4734	+ 1.3
38	199538	79.9756	- 1.3		50	200825	80.2724	+ 0.6
39	221726	85.0874	- 5.2		51	208551	82.0534	- 2.6
40	244938	90.4323	-13.1		52	225451	85.9453	- 6.9
41	244587	90.3515	-12.3		53	234256	87.9724	- 9.6
42	244444	90.3185	-13.0		54	243202	90.0325	-12.0
43	91962	54.3504	- 9.3		55	244280	90.2808	-10.8
44	91955	54.3486	-14.0		56	238368	88.9192	-10.1
45	192194	78.2807	- 1.3		57	127433	63.1108	- 5.7
46	213768	83.2552	- 3.7		58	244321	90.2902	- 9.9
47	235632	88.2892	- 8.9					
	Apparatus B							
82	158926	70.5587	- 1.5		89	123456	62.1538	- 4.0
83	244447	90.3192	-11.5		90	114338	59.9399	- 6.7
84	244456	90.3213	-12.7		91	244423	90.3137	-14.4
85	230304	87.0625	-10.0		92	252336	92.1368	-12.7
86	213741	83.2489	- 6.9		93	260803	94.0888	-15.3
87	200613	80.2236	- 5.4		94	269555	96.1081	-17.1
88	180035	75.4686	- 5.9					
	Apparatus C							
110	245917	90.6578	-18.2		120	91972	54.3530	---
111	246196	90.7221	-14.9		121	243494	90.0997	-16.1
112	189616	77.6851	- 1.7		122	91977	54.3542	---
113	189630	77.6884	- 0.5		123	7875.2	23.857	--
114	188945	77.5301	- 2.5		124	7881.0	23.862	---
115	188943	77.5296	- 1.7		125	53633	43.791	---
116	244066	90.2315	-15.4		126	7871.0	23.853	---
117	91961	54.3502	---		127	53643	43.794	---
118	91962	54.3504	-20.6		128	53655	43.797	---
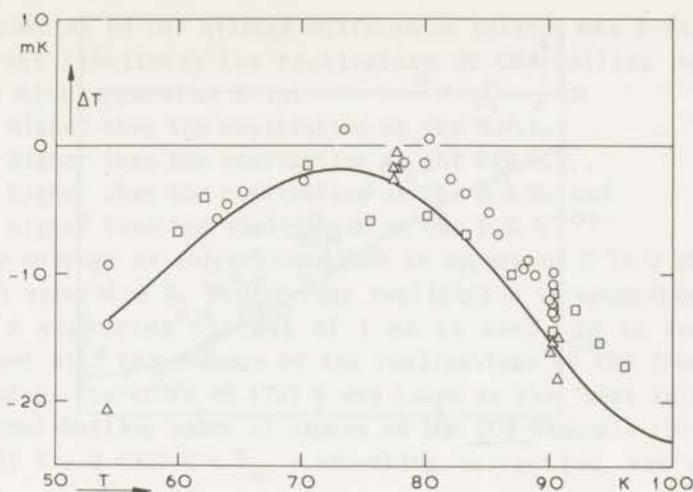
FIG. V-7

Differences between temperatures on the CCT-64 scale deduced from measurements with platinum thermometers and temperatures T_{pc} deduced from vapour pressures of liquid oxygen as obtained from our measurements. $\Delta T = T_{CCT-64} - T_{pc}$.

O measured with apparatus A
□ measured with apparatus B
△ measured with apparatus C.

For nearly all points in fig. V-7 the deviations from the curve are smaller than 5 mK and the average deviation is about 2.7 mK. The average deviation of the points in fig. V-8 from the curve is about 3 mK, but below 80 K the deviations of the points of Hoge are much larger.

This p,T relation is within the limits of accuracy consistent with the experimental values for the heat of vaporization and for the second virial coefficient as can be seen from fig. V-7, fig. II-1 and fig. II-3.

b. The boiling point of oxygen.

W values at the normal boiling point of oxygen according to the realizations of this point in different institutes were obtained for different thermometers in the same way as described
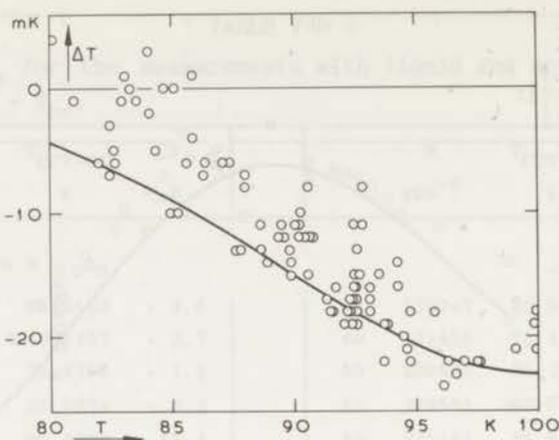
FIG. V-8

Differences between temperatures on the CCT-64 scale deduced from measurements with platinum thermometers and temperatures T_{pc} deduced from vapour pressures of liquid oxygen as obtained by Hoge [61] between 80 K and 100 K. $\Delta T = T_{CCT-64} - T_{pc}$.

for the hydrogen boiling point. These W values are collected in table V-E.

TABLE V-E

W values of different thermometers at the normal boiling point of oxygen as obtained at different institutes.

	$10^6 W_{NBS2}$	$10^6 W_{PSU3}$	$10^6 W_{PSU4}$	$10^6 W_{NPL3}$	Remarks
K.O.L.	243946	244021	244019	243775	Meas.No.83 and 91
N.P.L.	243939	244014	244015	243766	ref. 22
P.R.M.I.	243934	244009	244011	243757	ref. 23
N.B.S.	243944	---	---	---	declared value
P.S.U.	---	244005	244007	---	declared value

According to the average differences between the W values of different institutes the realization of the boiling point of oxygen with apparatus B is:

1.6 mK higher than the realization at the N.P.L.,

2.8 mK higher than the realization at the P.R.M.I.,

0.5 mK higher than the realization at the N.B.S. and

3.2 mK higher than the realization at the P.S.U.

The average of our realizations in apparatus C is 2 mK lower than in apparatus B. The average realization in apparatus C, in which a measuring current of 1 mA is used, is in very good agreement with the average of the realizations at the four other institutes. Therefore 90.1727 K was taken as the "best value" for the normal boiling point of oxygen on the CCT-64 scale (90.1727 K = 90.170 K + 0.0027 K = $\bar{T}_{nr}$ + smoothing correction, see section III-1).

c. The triple point of oxygen.

The average values for the temperature and the vapour pressure at the triple point of oxygen deduced from our measurements are given in table V-F together with values obtained by Hoge [61] and by Orlova [84].

In the calculation of a p,T relation for liquid oxygen adjusted to the CCT-64 scale the vapour pressure at the triple point has been taken equal to 1.099 mm Hg at 0°C and at standard gravity.

TABLE V-F

Temperatures and vapour pressures at the triple point of oxygen as obtained by different authors.

	T_{CCT-64} (K)	p (mm Hg)	Remarks
Hoge [61]	54.352	1.13 ± 0.01	5 meas., $T_{NBS-1939}$ = 54.363 K
Orlova [84]	54.355 ± 0.001	---	10 meas., T_{PRMI} = 54.368 K
This research	54.351 ± 0.003	1.099 ± 0.002	Table V-D, No. 43, 44, 117, 118, 120 and 122.

Since we used in our experiments thermometers from different institutes including the N.B.S. and the P.R.M.I., somewhat heavier

weight is given to the K.O.L. data and therefore the temperature
at the triple point of oxygen on the CCT-64 scale is taken to be
54.352 K.

d. The transition points in solid
   oxygen.

The temperatures at the transition points in solid oxygen
were determined in apparatus C. The procedure of these measure-
ments is described in section IV-4. The slow rise of the tempera-
ture of the block was observed from a few hundredths of a kelvin
below the transition temperature to a few hundredths of a kelvin
above this temperature. The transition temperatures were obtained
from graphs in which the measured resistance values were plotted
versus time.

For the transition near 24 K a typical curve is shown in fig.
V-9. Values of $1/(dR/dt)$ were obtained from the curve in fig. V-9
and plotted versus temperature in fig. V-10. It may be expected
that the curve in fig. V-10 is similar to the heat capacity ver-
sus temperature curve of solid oxygen near the transition point.
The heat capacity curve given by Hoge [61] has an analogous shape.
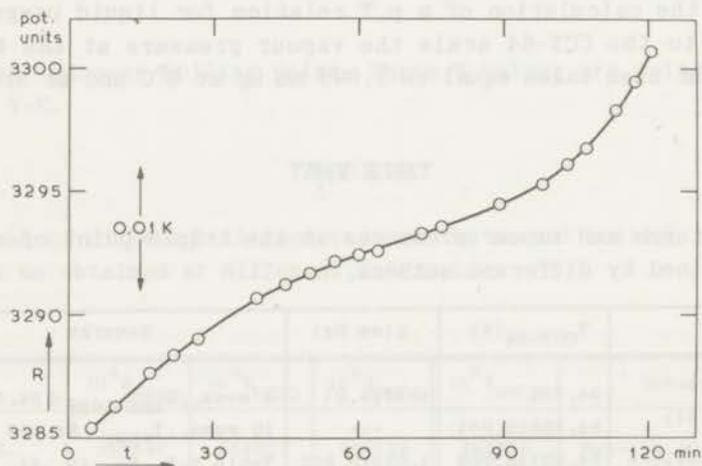Fagerstroem and Hollis Hallett [85] reported in 1966 results of

FIG. V-9

Resistance of a platinum thermometer versus time during the pas-
sage of the transition point in solid oxygen at 23.86 K.

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measurements of the specific heat of oxygen from liquid helium temperatures up to about 70 K. They observed near 24 K a λ-like peak in the specific heat versus temperature curve with no evidence of a latent heat. Usually the temperature at which the heat capacity has its maximum value is taken as the transition point temperature. Fagerstroem and Hollis Hallett measured the temperatures with a carbon resistance thermometer and did not claim a better accuracy for the measured temperature than 0.1 percent.
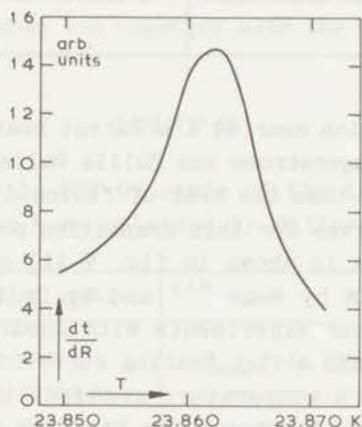

FIG. V-10

(dt/dR) versus T deduced from the smoothed curve in fig. V-9. The curve of (dt/dR) versus T resembles the curve of C_s versus T.

Hoge [61] and Orlova [84] determined the temperature at this transition point accurately with platinum resistance thermometers. Their results and the average of our results obtained in apparatus C are given on the CCT-64 scale in table V-G.

From the data in table V-G the value 23.860 K may be taken as the "best value" for the transition point temperature on the CCT-64 scale. Because of the absence of a latent heat and the small temperature interval between this transition point and the boiling point of hydrogen this transition point is not very suitable as a fixed point for the calibration of platinum thermometers.

TABLE V-G

The temperature on the CCT-64 scale of the transition point in
solid oxygen near 24 K as obtained by different authors.

	$T_{CCT-64}(K)$	Remarks
Hoge [61]	23.878	$T_{NBS-1939} = 23.886$ K
Orlova [84]	23.861±0.002	5 measurements, $T_{PRMI} = 23.876$ K
This research	23.858±0.004	3 measurements, No. 123, 124 and 126.

For the transition near 44 K a latent heat of 749 joules per
mole was found by Fagerstroem and Hollis Hallett [85]. This latent
heat is even larger than the heat of fusion of oxygen. Neverthe-
less the heating curves for this transition point are not flat in
our experiments (as is shown in fig. V-11) and also not in the
earlier experiments by Hoge [61] and by Orlova [84]. It may be
mentioned that in our experiments with apparatus C it was also
not possible to obtain a flat heating curve for the triple point.
This may be due to a temperature gradient between the thermo-
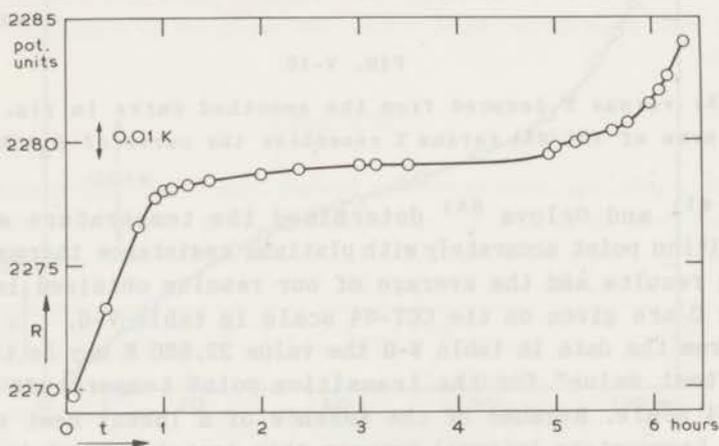meters and the oxygen in the vapour pressure thermometer. In the

FIG. V-11

Resistance of a platinum thermometer versus time during the pas-
sage of the transition point in solid oxygen at 43.8 K.

experiments of Hoge and of Orlova there was a possibility that
the heat contact between the solid oxygen and the copperblock was
not sufficient because the vapour pressure of oxygen at 44 K is
below 0.015 mm Hg. In our experiments some helium gas was admitted
to the vapour pressure thermometer at 20 K. The value of the
temperature at the transition for our experiments was taken from
the resistance value of the thermometer at the first sharp de-
flection of the heating curve just as was done for the triple
point measurements in apparatus C. The average of our results
obtained in apparatus C for the temperature at this transition
point is given in table V-H together with the results obtained by
Hoge and by Orlova.

TABLE V-H

The temperature on the CCT-64 scale of the transition point in
solid oxygen near 44 K as obtained by different authors.

	$T_{CCT-64}(K)$	Remarks
Hoge [61]	43.796	T_{NBS} = 43.800 K.
Orlova [84]	43.802±0.002	5 measurements, T_{PRMI} = 43.818 K.
This research	43.794±0.003	3 measurements, No. 125, 127 and
		128.

Orlova takes for the temperature at this transition the
value at the time that the transition is half-way completed.
Since the total temperature rise during the transition was about
13 mK, the reported value might be 6 or 7 mK too high. Taking
this into account the value 43.795 K is recommended as the "best
value" for the temperature on the CCT-64 scale at this transition.
From these results it may be concluded that the techniques to
calibrate thermometers at this transition point still need im-
provement.

CHAPTER VI

ON THE CALIBRATION OF PLATINUM THERMOMETERS BELOW 91 K

1. Comparison of different methods for the interpolation of differences of the resistance ratios of platinum thermometers between 91 K and 12 K.

The method to obtain ΔW values between 90 K and 14 K by interpolation between the ΔW values obtained experimentally at a number of fixed points which is adopted in the recommendations for the new IPTS (see section III-2) is chosen from a number of possible methods that were proposed by several authors.

In 1966 Lovejoy's first proposal [29] to interpolate ΔW values was checked at the K.O.L. [66] with the data for four of the thermometers which were used for the comparison of the national scales [22, 23]. This interpolation method did not give a sufficiently accurate result. As somewhat more accurate alternatives Lovejoy suggested to use two different interpolation formulae below 54 K (see ref. 86) and, independently, Durieux et al. [66] suggested to divide the range from 54 K to 14 K into two parts and to use an additional calibration point at about 17 K. This last proposal was adopted in the provisional recommendations of the Working Groups of the C.C.T. in Moscow in 1966.

To check the merits of different interpolation methods for ΔW values below 91 K we compared three of these methods. The results of this comparison were reported to the C.C.T. in June 1967 [87]. The three methods that were compared are:

1. The method recommended by the Working Groups of the C.C.T. in Moscow in 1966:

between 90 K and 54 K: $\Delta W = a_1 + b_1 T + c_1 T^2$, constants to be determined from calibrations at 90 K and 54 K and from $d\Delta W/dT$ at 90 K;

between 54 K and 20 K: $\Delta W = a_2 + b_2 T + c_2 T^2$, constants to be determined from calibrations at 54 K and 20 K and from $d\Delta W/dT$ at 54 K;

TABLE VI-A

Data for W of several platinum thermometers, selected from the scale comparison data, which were used to check the interpolation methods for $\triangle W$. A: measured at the N.P.L., B: measured at the P.R.M.I. Points marked with an asterisk are used to calculate the constants in the interpolation formulae.

T_{CCT-64} K	$\overline{W}$ x 10^6	$W_{PSU4}-\overline{W}$ x 10^6	$W_{NBS2}-\overline{W}$ x 10^6	$W_{NPL3}-\overline{W}$ x 10^6	$W_{T2}-\overline{W}$ x 10^6	
90.2703	244234.4	201.8	124.8	−46.4	−114.9	*, A
72.6640	167953.9	216.5	137.5	−51.7	−122.8	B
55.7169	97332.4	224.5	155.2	−57.1	−131.7	*, A
41.2103	45401.3	227.3	166.4	−56.1	−140.1	B
30.0985	17366.9	223.3	178.0	−51.3	−148.4	B
22.9716	6904.6	218.9	187.2	−44.2	−158.4	A
20.3331	4528.6	216.8	189.7	−39.1	−163.7	*, B
17.9436	2985.2	213.5	191.2	−35.5	−166.8	*, A
15.6424	1960.1	209.8	190.0	−32.0	−168.2	A
14.0664	1473.1	205.7	188.2	−29.8	−167.7	*, A
12.022	1048.1	199.7	184.3	−28.0	−164.7	A
$(d \triangle W/dT)_{90.3}$		−1.159	−0.716	+0.266	+0.660	K^{-1}

TABLE VI-B

Data obtained at the K.O.L. which were used to check the interpolation methods for $\triangle W$.

T_{CCT-64} K	$10^6(W_{145}-W_{T4})$	$10^6(W_{153}-W_{T4})$	$10^6(W_{143}-W_{T4})$	
90.5	88	112	159	*
77.5	94	120	169	
54.35	107	133	183	*
43.88	113	135	194	
23.04	151.0	139.3	222.8	
20.4	160.0	140.9	230.4	*
18.05	167.2	143.1	235.4	
17.03	169.7	143.8	236.7	*
15.34	172.1	144.0	237.7	
13.80	172.9	143.4	236.0	*
$(d \triangle W/dT)_{90.5}$	−0.505	−0.643	−0.913	K^{-1}

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between 20 K and 14 K: $\triangle W = a_3 + b_3 T + c_3 T^2 + d_3 T^3$, constants to be determined from calibrations at 20 K, 17 K and 14 K and from $d\triangle W/dT$ at 20 K;

2. The same method as mentioned under 1 but without a calibration point at 17 K. Between 20 K and 14 K is used: $\triangle W = a_3' + b_3' T + c_3' T^2$;

3. Between 90 K and 54 K: the same as method 1;

   between 20 K and 14 K: $\triangle W = a_3'' + b_3'' T + c_3'' T^2$, constants to be determined from calibrations at 20 K, 17 K and 14 K;

   between 54 K and 20 K: $\triangle W = a_2' + b_2' T + c_2' T^2 + d_2' T^3$, constants to be determined from calibrations at 54 K and 20 K and from $d\triangle W/dT$ at 54 K and 20 K.

The second method is a simplification of the first. In the third method we made the interpolation below 20 K independent from the interpolation at higher temperatures. This last method was included in the recommendations of the C.C.T. in September 1967.

The comparison of the interpolation methods has been made using data for four thermometers selected from the results of the scale comparisons at the N.P.L. and at the P.R.M.I. and data for four other thermometers obtained with apparatus C. No data of fixed point calibrations were used because data from comparisons of thermometers can better be used to check interpolation methods. In this way uncertainties due to errors in the realization of the fixed points are avoided.

In the tables VI-A and VI-B the experimental information used in the calculations is given. The data in table VI-A for the thermometers PSU4, NBS2, NPL3 and T2 are taken from ref. 22 and ref. 23. The T values and $\overline{W}$ values are those given in ref. 24. The data were selected from the complete information in order to limit the number of calculations and to exclude data which are apparently less accurate. The data in table VI-B are taken from table IV-D. The data marked with an asterisk are used as calibration points, the other data being used to check the interpolation formulae.

In the tables VI-C and VI-D the values of $T_m - T_c = (\triangle W_{measured} - \triangle W_{calculated})(dT/dW)$ are given for the three interpolation methods. The results are also shown in fig. VI-1 and fig. VI-2. The curves in the graphs are somewhat arbitrary since only a small number of data has been used. The influence of an error of 1×10^{-6} in $\triangle W$ on the temperature ($10^{-6} dT/dW$) is shown in fig. VI-1. Interpolation method 3 gives the most consistent results.

TABLE VI-C and TABLE VI-D

Comparison of three different interpolation methods for ΔW. The temperature differences $\Delta T = T_m - T_c$ show the accuracy of the interpolation according to procedure 1, 2 or 3.

T K	ΔT_{PSU4} mk	ΔT_{NBS2} mk	ΔT_{NPL3} mk	ΔT_{T2} mk	Procedure
72.66	−0.3	−0.3	−0.1	+0.5	1, 2, 3
41.21	+0.9	−1.1	+0.3	−0.1	1, 2
	−0.4	−0.9	+0.5	−0.4	3
30.10	+0.8	−1.4	−0.6	+1.3	1, 2
	−0.8	−0.9	−0.2	+0.6	3
22.97	+0.6	−0.2	−1.5	+1.4	1, 2
	−0.7	+0.3	−1.3	+0.9	3
15.64	−3.4	−1.4	−0.3	−0.3	1
	−0.3	+0.3	+0.8	−1.4	2
	+1.7	+0.8	+0.3	−0.8	3
12.02	−26.0	+13.0	0.0	+0.6	1
	+5.0	−1.9	−10.0	+12.4	2
	−3.7	−4.3	−6.8	+8.7	3

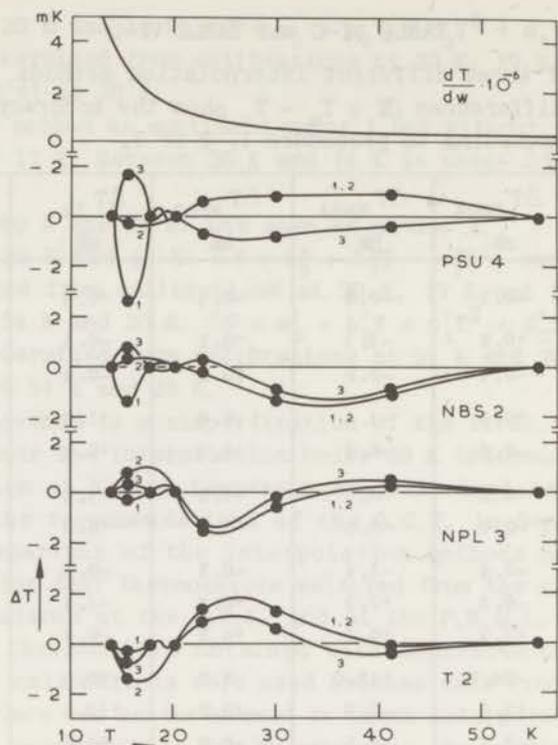| T K	ΔT_{145} mk	ΔT_{153} mk	ΔT_{143} mk	Procedure
77.5	0	0	−0.2	1, 2, 3
43.88	−0.9	−0.6	+1.2	1, 2
	0	+0.3	+1.5	3
23.04	−2.3	−1.6	−1.4	1, 2
	+0.5	+1.3	−0.4	3
18.05	+0.5	+0.7	0	1
	+3.1	+3.5	+1.1	2
	−0.5	−0.5	−0.4	3
15.34	−2.1	+0.3	+0.6	1
	+4.4	+5.0	+3.5	2
	−0.3	0	+1.5	3

FIG. VI-1

Differences between W values obtained experimentally and W values
obtained by interpolation with the methods 1, 2 and 3 for differ-
ent thermometers, expressed in temperature differences.

$\Delta T = (W_{measured} - W_{calculated})(dT/dW)$.

The maximum differences between temperatures calculated from
measured W values for different thermometers using method 3 are
2.5 mK between 14 K and 20 K, 2 mK between 20 K and 54 K and 1 mK
between 54 K and 90 K. These differences are only a slightly lar-
ger than the inaccuracies in the experimental data.

The extrapolation down to 12 K can give errors of 0.01 K for
the interpolation method 3. This uncertainty is the same as the
uncertainty of the interpolation method described in section VI-2.

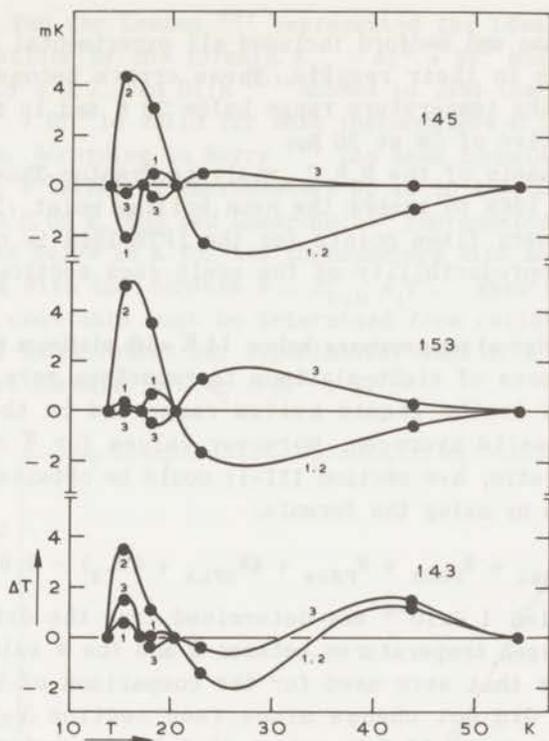The results obtained from method 2 between 14 K and 20 K for

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FIG. VI-2

Differences between W values obtained experimentally and W values
obtained by interpolation with the methods 1, 2 and 3 for differ-
ent thermometers, expressed in temperature differences.
$\Delta T = (W_{measured} - W_{calculated})(dT/dW)$.

the thermometers 145, 153 and 143 show that the omission of the
calibration point at 17 K can introduce errors of 4 to 5 mK.

Preston-Thomas and Bedford [86] analyzed the interpolation of
ΔW values between fixed points using data of 48 thermometers in
total. The results of their analysis were presented to the C.C.T.
in September 1967. They also considered our interpolation method
3 as the best one, but they found somewhat larger deviations for
the thermometers used for the comparison of the national scales
because they used all measured points in their calculation. Thus

Preston–Thomas and Bedford included all experimental errors in ΔW measurements in their results. These errors become especially visible in the temperature range below 20 K and in the temperature derivative of ΔW at 20 K.

On the basis of the N.R.C. analysis Preston–Thomas proposed in February 1968 to insert the neon boiling point (27 K) in the list of primary fixed points for the IPTS–1968 in order to improve the reproducibility of the scale (see section III–2).

2. Determination of temperatures below 14 K with platinum thermometers.

Resistances of eight platinum thermometers were measured in apparatus B in the liquid helium range and in the ranges of liquid and solid hydrogen. Moreover values for $\overline{W}$ (the average resistance ratio, see section III–1) could be obtained from these measurements by using the formula:

$$\overline{W} = \frac{1}{12} \left(2W_{NBS2} + W_{PSU3} + W_{PSU4} + 4W_{NPL3} + 4W_{T2}\right) - 1.9 \times 10^{-6}.$$

The correction 1.9×10^{-6} was determined from the differences at liquid hydrogen temperatures between $\overline{W}$ and the W values of those thermometers that were used for the comparison of the national scales and did not change since (see section V–1). For the measured points at 11.7 K and at 10.5 K temperatures were deduced by extrapolation of the CCT–64 table and below 5.1 K temperatures were deduced from vapour pressures of liquid helium by using the T_{58} scale.

From the results of these measurements we tried to find a relation between the resistance ratio of a thermometer and the temperature which is accurate within a few hundredths of a kelvin.

For temperatures higher than 14 K it is possible to interpolate accurately between W differences obtained at a few calibration temperatures. Therefore also for the lower temperature range we plotted the differences in W values of different thermometers versus temperature. As can be seen from fig. VI–3, in which a typical ΔW curve is drawn, such a curve can have a maximum or a minimum value at about 8 K. It seems impossible in this temperature range to interpolate accurately between measured ΔW values when using a low degree polynomial.

One can also try to find independently for each thermometer the relation between the resistance ratio and the temperature. This was done earlier by several authors.

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In 1940 Van der Leeden [88] represented the ideal resistance ratio of platinum by the formula $W_{id} = AT^2 + BT^n$ and found for n the value 4.5 ± 0.3. Van Dijk [89] showed in 1964 that the formula $W = W_0 + AT^2 + BT^5$ is valid for most thermometers at liquid helium temperatures. According to Berry [90] the same formula can be used to represent W values of thermometers up to 10 K with an accuracy of 0.03 K to 0.05 K. Kos and Lamarche [91] represented the experimental values below 16 K for two thermometers with an accuracy of about 0.01 K with the formula $W = \sum_{i=0}^{5} A_i T^i$. When this formula is used six constants must be determined from calibration data.

We tried to represent our experimental data of W and T by the four constant formula: $W = W_0 + AT^2 + BT^\gamma$.
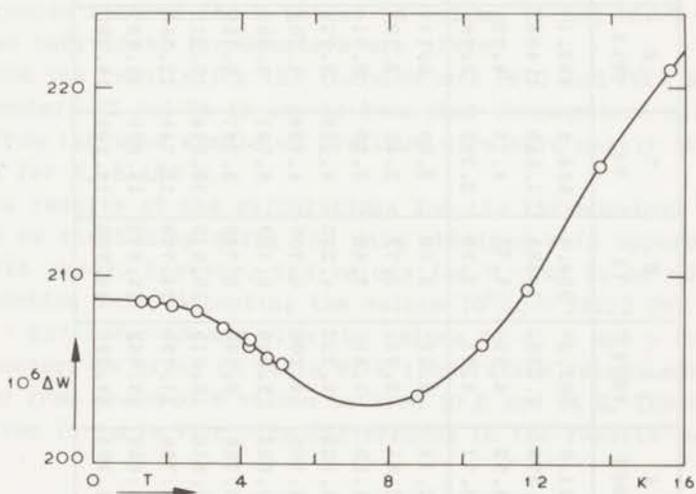

FIG. VI-3

$W_{NBS2} - W_{NPL3}$ according to measurements with apparatus B below 15 K.

The constants were determined in the following way:
Provisional values for W_0 and A were determined from a straight line drawn through the points at the four temperatures below 3 K (table IV-C, No. 60, 61, 62 and 63) in a graph of W vs T^2. The values of $\log(W-W_0-AT^2)$ for the points between 2 K and 12 K were plotted versus log T. It was not possible to represent these

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TABLE VI-E

Temperatures calculated from measured W values below 14.3 K with the formula $W = W_0 + AT^2 + BT^\gamma$.

1	2 $\overline{W}$	3 NBS2	4 PSU3	5 PSU4	6 T2	7 T4	8 NPL3	9 LN	10 B2	11 T(K)	12 $\Delta T_{max.}$(mK)
$10^6 W_0$	509.5	691.3	701.9	705.2	354.7	354.5	482.1	638.6	496.2		
$10^6 A$	1.428	1.275	1.275	1.275	1.555	1.555	1.465	1.32	1.51		
γ	4.61	4.52	4.52	4.52	4.75	4.75	4.62	4.57	4.71		
$10^9 B$	3.50	4.69	4.71	4.71	2.30	2.295	3.36	4.00	2.66		
62.	2.10	2.11	2.11	2.11	2.08	2.09	2.11	2.09	2.08	2.097	20
63.	2.80	2.82	2.81	2.81	2.79	2.80	2.79	2.80	2.80	2.807	20
64.	3.51	3.52	3.52	3.51	3.49	3.50	3.51	3.52	3.51	3.509	20
65.	4.227	4.230	4.222	4.222	4.225	4.218	4.221	4.221	4.225	4.224	6
66.	4.709	4.696	4.706	4.700	4.709	4.704	4.709	4.696	4.714	4.705	9
67.	5.094	5.085	5.088	5.088	5.103	5.091	5.090	5.080	5.100	5.092	12
76.	8.749	8.752	8.750	8.760	8.749	8.747	8.759	8.747	8.746	8.751	9
75.	10.512	10.514	10.516	10.515	10.519	10.514	10.515	10.512	10.507	10.514	7
74.	11.747	11.747	11.756	11.753	11.746	11.745	11.750	11.748	11.751	11.749	7
73.	13.664	13.658	13.658	13.662	13.672	13.670	13.667	13.675	13.658	13.665	10
68.	14.297	14.287	14.291	14.290	14.308	14.309	14.300	14.304	14.285	14.297	12

points accurately by a straight line but provisional values for γ and B could be obtained. With these values for γ and B the values for W_0 and A could be adjusted. With these adjusted values final values for γ and B were obtained. A final slight adjustment of the values for W_0 and A completed the calculation.

In table VI–E the values for the constants W_0, A, B and γ are given for each of the thermometers and for $\overline{W}$, and the calculated temperature values are given for all points between 2 K and 14.3 K. The numbers in column 1 correspond to the numbers in the first column of table IV–C. The T values below 5.1 K in column 11 are calculated from the measured vapour pressure of helium; at the higher temperatures they are the averages of the T values of all thermometers. In column 12 the absolute values of the largest differences between the T values in column 11 and the T values for the individual thermometers are given.

From the results for the thermometers PSU3 and PSU4 and the thermometers T2 and T4 it can be seen that thermometers which are made from the same sample of platinum wire have nearly the same values for A, B and γ.

The results of the calculations for the thermometers T4 and LN can be checked by using the data obtained with apparatus A. For this check, however, the values for W_0 had to be adjusted (see section V–1). Accepting the values $10^6 W_0 = 351.2$ for T4 and $10^6 W_0 = 637.1$ for LN and with the values of A, B and γ for both thermometers as given in table VI–E temperature values were calculated from measured W values between 10 K and 14 K. The results are given in table VI–F. The differences in the results for both

TABLE VI–F

Temperatures below 14 K obtained from measured W values of the thermometers T4 and LN with apparatus A.

	T_{T4}(K)	T_{LN}(K)	$\triangle$ T (mK)
31.	9.913	9.913	0
30.	11.032	11.026	6
29.	12.093	12.090	3
28.	13.051	13.047	4
32.	13.799	13.798	1

thermometers are just as small as the differences in the results for those thermometers as given in table VI–E.

The constants in the formula $W = W_0 + AT^2 + BT^\gamma$ were also determined for the thermometer Pt 1 for which experimental data were obtained by De Boer [92] in 1935 and for the thermometer 320 for which experimental data were given by Berry [90] in 1967.

The constants for the thermometer Pt 1 are:
$10^6 W_0 = 362.3$; $10^6 A = 1.365$; $\gamma = 4.34$ and $10^9 B = 7.15$
and the constants for the thermometer 320 are:
$LO^6 W_0 = 434.5$; $10^6 A = 1.24$; $\gamma = 4.64$ and $10^9 B = 3.24$.

The temperature values that were calculated from the formula $W = W_0 + AT^2 + BT^\gamma$ using the experimental W values and the data for W_0, A, B and γ given above are mainly within 0.02 K equal to the gas thermometer temperatures between 2 K and 14 K. A larger deviation is found only for one point below 10 K for the thermometer Pt 1 that was not very accurate (c.f. Kos and Lamarche [91]) and for the point at 14 K for Pt 1, suggesting that for this thermometer there are significant deviations from this formula already at 14 K.

The conclusion may be drawn from this analysis that it is possible to describe the calibration of platinum thermometers by the formula $W = W_0 + AT^2 + BT^\gamma$ in such a way that the temperatures calculated for different thermometers are the same within 0.02 K between 4 K and 14 K. To find adequate values for the constants W_0, A, B and γ it is desirable that a thermometer be calibrated at a few temperatures between 10 K and 14 K and at a few temperatures in the liquid helium range including one or two points above 4.2 K.

The results suggest that platinum thermometers can be used for temperature measurements below 14 K without calibrations between 5 K and 10 K with an agreement of the results for dif - ferent thermometers within 0.02 K when the formula $W = W_0 + AT^2 + BT^\gamma$ is used for the interpolation between calibration temperatures.

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SAMENVATTING

De onderzoekingen die in dit proefschrift beschreven worden hebben enerzijds betrekking op de bepaling van de relatie tussen de dampspanning van vloeibare zuurstof en de temperatuur (p,T-relatie) zowel door berekening met behulp van een formule uit de thermodynamica als langs directe experimentele weg en anderzijds op de ijking van – en de temperatuurmeting met platina-weerstands-thermometers beneden 100 K.

In hoofdstuk I wordt naast een algemene inleiding en een overzicht van dit onderzoek ook een overzicht gegeven van de voornaamste ontwikkelingen in de temperatuurmeting met platina-weerstandsthermometers sinds 1900.

In hoofdstuk II wordt uit de beschikbare gegevens betreffende de thermodynamische eigenschappen van zuurstof een keuze gedaan. De met de verkozen waarden berekende dampspanning (p) van vloei-bare zuurstof bij een aantal temperaturen (T) tussen 54 K en 100 K (tabel II-B) wordt beschreven door een vergelijking waarin log p gelijkgesteld is aan een vijfterm in T. Deze beschrijving wordt vergeleken met metingen en berekeningen van andere onder-zoekers (fig. II-7, II-8 en II-9). Met gebruikmaking van dezelfde gegevens voor de thermodynamische eigenschappen wordt de verdam-pingswarmte van vloeibare zuurstof als functie van de temperatuur berekend voor temperaturen tussen 55 K en 100 K (tabel II-C) en de resultaten van deze berekening worden vergeleken met experi-mentele bepalingen van deze verdampingswarmte (fig. II-10).

Hoofdstuk III bevat details omtrent twee temperatuurschalen voor platinathermometers voor temperaturen beneden 0°C (de CCT-64-schaal en de voorgestelde Internationale Praktische Tempera-tuurschaal van 1968). Bovendien worden de verschillen tussen de belangrijkste temperatuurschalen voor platinathermometers voor temperaturen tussen 10 K en 91 K gegeven.

In hoofdstuk IV worden de drie enigszins verschillende appa-raten besproken, die gebruikt zijn voor de vergelijking van platina-weerstandsthermometers met dampspanningsthermometers waarvan het reservoir vloeibare zuurstof, waterstof of helium

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bevat. De methoden die gebruikt zijn voor de weerstandsmeting en
de drukmeting worden besproken en de directe meetresultaten wor-
den vermeld.

In hoofdstuk V worden temperaturen die berekend kunnen worden
uit de gemeten weerstanden van geijkte weerstandsthermometers
vergeleken met temperaturen die berekend kunnen worden uit de ge-
meten dampspanningen van waterstof en zuurstof. Temperaturen wer-
den uit de weerstandsmetingen bepaald volgens de CCT-64-schaal.
Uit de gemeten dampspanningen van vloeibare waterstof werden tem-
peraturen berekend met behulp van de in 1960 in Leiden afgeleide
p,T-relatie voor evenwichtswaterstof; deze temperaturen worden
aangeduid met T_{L60}. Bij de vergelijking van temperaturen op de
L60 schaal met temperaturen op de CCT-64-schaal wordt tevens de
goede overeenstemming van onze metingen met die van Hoge en
Arnold en met die van Barber en Miss Horsford getoond (fig. V-6).
Een door Ter Harmsel berekende p,T-relatie voor evenwichtswater-
stof, die is aangepast aan de waarden van T bij het kookpunt en
het tripelpunt volgens de voorgestelde IPTS-1968, wordt vermeld.
Uit de gemeten dampspanningen van vloeibare zuurstof werden tem-
peraturen berekend volgens de p,T-relatie die afgeleid is in
hoofdstuk II. Deze worden vergeleken met temperaturen op de CCT-
64-schaal, waarbij de goede overeenstemming van onze metingen met
die van Hoge tussen 80 K en 100 K wordt getoond (fig. V-7 en
V-8). Op grond van deze vergelijking van temperatuurwaarden, af-
geleid uit de druk, met temperaturen op de CCT-64-schaal is een
p,T-relatie voor vloeibare zuurstof afgeleid voor welke tempera-
turen uit gemeten drukken zo goed mogelijk gelijk zijn aan tempe-
raturen op de CCT-64-schaal. Speciale aandacht wordt besteed aan
de overeenstemming in de realisatie van de kookpunten van water-
stof en zuurstof in verschillende laboratoria en aan de bepaling
van de temperaturen van de tripelpunten van waterstof en zuurstof
en van de twee overgangspunten in vaste zuurstof.

In hoofdstuk VI wordt enerzijds aandacht besteed aan de
interpolatie van verschillen in de gereduceerde weerstand W
($= R(T)/R(0°C)$) van platina-weerstandsthermometers in het tempe-
ratuurgebied van de IPTS-1968 beneden 91 K en anderzijds wordt
de nauwkeurigheid van de interpolatie van de gereduceerde weer-
stand van verschillende platina-thermometers met de formule
$W = W_0 + AT^2 + BT^\gamma$ beneden 14 K volgens onze metingen in vloei-
baar helium en in vaste waterstof onderzocht.

Teneinde te voldoen aan de wens van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

In 1956 behaalde ik het einddiploma H.B.S.-B aan het Gemeentelijk Dalton Lyceum te Den Haag, waarna ik mijn studie aan de Rijksuniversiteit te Leiden begon. In december 1959 legde ik het kandidaatsexamen af in de natuurkunde en wiskunde met bijvak scheikunde. Na de vereiste tentamens in de theoretische natuurkunde en de mechanica te hebben afgelegd bij Prof. Dr S.R. de Groot, Prof. Dr J.A.M. Cox en Prof. Dr P. Mazur en een tentamen bij Prof. Dr J.A. Goedkoop volgde in maart 1963 het doctoraalexamen in de experimentele natuurkunde, waarbij ik tevens de bevoegdheid tot het geven van middelbaar onderwijs in de natuurkunde en de mechanica verwierf.

Mijn praktische opleiding aan het Kamerlingh Onnes Laboratorium begon in januari 1960 toen ik medewerker werd van de afdeling voor thermometrie die onder leiding stond van Dr H. van Dijk. Tot mijn doctoraalexamen bestond mijn werk hier voornamelijk uit het ijken van thermometers en de verdere ontwikkeling van de daartoe benodigde apparatuur, alsmede uit enig voorbereidend werk voor het onderzoek dat in dit proefschrift beschreven is. Dit onderzoek is onder toezicht van Dr H. van Dijk en Dr M. Durieux uitgevoerd, waarbij de leiding van de afdeling voor thermometrie sinds 1965 berustte bij Dr M. Durieux.

Vanaf februari 1961 vervul ik een taak als assistent op het practicum voor voorkandidaten. In december 1967 werd ik belast met de leiding van het natuurkundig practicum voor studenten in de medicijnen. In januari 1965 werd ik benoemd tot wetenschappelijk ambtenaar en in januari 1967 tot wetenschappelijk medewerker.

Sinds september 1965 assisteer ik onder leiding van Drs C. van Rijn bij het natuurkundig practicum van het Gemeentelijk Instituut voor opleidingen in de exacte vakken van de gemeente 's-Gravenhage.

Bij mijn metingen heb ik in de beginfase samengewerkt met Dr M.R.M. Moussa, die medio 1966 naar Egypte terugkeerde. Bij het terzelfdertijd meten van weerstanden en drukken hebben de heren E.H. Vossepoel en H. Kossen mij vaak de helpende hand gereikt. Later heb ik enige tijd hulp gehad van de heer H. Fredrikze. Berekeningen werden op het Mathematisch Instituut der Universiteit voor mij verricht door Dr W.H. Nuy en Drs J.A. Dorrepaal. Discus-

sies met Dr H. ter Harmsel en Drs C. van Rijn zijn voor mij zeer
waardevol geweest. Veel medewerking heb ik ook ondervonden van de
technische en de administratieve staf van het Kamerlingh Onnes
Laboratorium. De metalen apparatuur werd onder leiding van de
heer L.W. Muller vervaardigd. Het glazen gedeelte der apparatuur
werd vervaardigd onder leiding van de heer H. Kuipers. Van de
cryogene staf heb ik in het bijzonder hulp gehad van de heren
L. Neuteboom, J. Turenhout en J. Sprong. De tekeningen in dit
proefschrift werden verzorgd door de heer W.F. Tegelaar. Bij het
corrigeren van de engelse tekst van dit proefschrift kreeg ik
hulp van mej. M.M. van Vliet.

STELLINGEN

I

Uit metingen tussen 70 K en 90 K van de weerstand van een zogenaamde "long-stem" platinathermometer, die geijkt is voor het temperatuurgebied boven 90 K volgens de voorschriften van de voorgestelde Internationale Praktische Temperatuurschaal van 1968, kan de temperatuur worden bepaald door extrapolatie van de voor hogere temperaturen bepaalde formule voor de verschillen tussen de gereduceerde weerstandswaarden van de thermometer en de referentietabel. De op deze wijze bereikbare nauwkeurigheid is in het algemeen beter dan 0.01 K.

II

Voor de berekening van thermomoleculaire drukverschillen is de door Bennett en Tompkins gemodificeerde empirische formule van Chu Liang meer geschikt dan de semi-empirische formules van Weber.

> S. Chu Liang, J. appl. Phys. 22 (1951) 148
> M.J. Bennett en F.C. Tompkins, Trans. Farad. Soc. 53 (1957) 185.
> S. Weber, Commun. Kamerlingh Onnes Lab., Leiden No. 246c en Suppl. No. 71b.

III

De spin-roosterrelaxatie in $Mn(NH_4)_2(SO_4)_2.6H_2O$ kan worden beschreven als een quasi-ramanproces. Volgens De Vries e.a. is daarbij de relaxatietijd bij lage temperatuur evenredig met T^{-7}. Een evenredigheid van de relaxatietijd met T^{-5} is echter in betere overeenstemming met de experimentele resultaten van De Vries en dit mag ook worden verwacht.

> A.J. de Vries, J.M.W. Livius, D.A. Curtis, A.J. van Duyneveldt en C.J. Gorter, Commun. Leiden No. 356a.

IV

Sommige van de door Ferreira da Silva gemeten opwarmingscurven ter bepaling van de warmtecapaciteit van een niobiumpreparaat vertonen een knik. Voor deze metingen kunnen de waarden voor de warmtecapaciteit ter weerszijden van de knik worden bepaald zonder de door Ferreira da Silva gebruikte onderstelling.

> J. Ferreira da Silva, Proefschrift, Leiden, 1967, paragraaf 4.2.5.4.

V

De experimentele aanvangssusceptibiliteit van een ferromagnetisch preparaat wordt niet alleen bepaald door de demagnetiserende factor.

VI

De bewering van Klein e.a. dat de klasse van 3-dimensionale tensoren van de vierde orde een basis heeft van twintig lineair onafhankelijke irreducibele tensoren is onjuist.

> Wm.M. Klein, D.K. Hoffman en J.S. Dahler,
> External field dependence of transport
> properties I, Department of Chemical
> Engineering, University of Minnesota,
> Minneapolis, Minnesota.

VII

Het gebruik dat Haywood maakt van de term "scale-temperature" bevordert het opheffen van onduidelijkheden in de nomenclatuur van temperaturen en temperatuurschalen niet.

> R.W. Haywood, Proc.Inst.Mech. Engineers,
> Vol. 182, Part 1, verschijnt binnenkort.

VIII

De verklaring die Gunter en Jeffries geven van de door hen gevonden veldafhankelijkheid van de kernspin-roosterrelaxatietijd in $La_2Mg_3(NO_3)_{12}.24H_2O$ met 1% Nd is onjuist.

> T.E. Gunter en C.D. Jeffries, Phys. Rev.
> 159 (1967) 290.

IX

Afschaffing van het systeem van de zogenaamde "no-claim" korting op de premie van verzekeringen tegen wettelijke aansprakelijkheid kan er toe bijdragen dat het aantal verkeersdeelnemers dat zich na het beschadigen van geparkeerde voertuigen aan de vergoeding van deze schade tracht te onttrekken vermindert.

X

Bij voetbal kan de bal bij een goed genomen strafschop door de keeper niet uit het doel worden gehouden.

R. MUIJLWIJK   Leiden, 4 juli 1968