

# On the extension of the international temperature scale down to about 20 degrees K : using platinum resistance thermometry

**Author:**

Lowenthal, Gerhard Clause

**Publication Date:**

1957

**DOI:**

<https://doi.org/10.26190/unsworks/7403>

**License:**

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/61887> in <https://unsworks.unsw.edu.au> on 2024-04-25

ON THE EXTENSION OF THE  
INTERNATIONAL TEMPERATURE  
SCALE DOWN TO ABOUT  $20^{\circ}\text{K}$

(USING PLATINUM RESISTANCE THERMOMETRY)



A Thesis submitted by G. C. Lowenthal  
to gain the degree of Master of Science  
in the New South Wales University of  
Technology, School of Applied Physics.

.....

UNIVERSITY OF N.S.W.

27905 26.FEB.75

LIBRARY

The author certifies herewith that no part of the material contained in this thesis has ever been submitted by him for a higher degree to any other University or similar Institution.



## S U M M A R Y

Apparatus and methods are described for temperature measurements with five platinum resistors of differing purity in the ranges  $14^{\circ}$  to  $22^{\circ}\text{K}$  and  $54^{\circ}$  to  $90^{\circ}\text{K}$ .

Results are analysed together with all results of available published work in order to find a calibration procedure which will provide a simple and precise temperature scale.

This aim can be attained between  $90^{\circ}$  and  $20^{\circ}\text{K}$  in terms of a Standard Platinum Scale (SPS) such as that recently published in Procès-Verbaux des Séances du Comité-Internationale des Poids et Mesures (1954, Vol.24, p.T142/143). Given calibrations at the normal boiling points of oxygen ( $90.19^{\circ}\text{K}$ ) and neon ( $27.07^{\circ}$ ) and platinum so pure that its  $\alpha$  exceeds 0.003920, this scale ( $Y_T$ ) can be reproduced between these temperatures to within a few millidegrees using the so-called Cragoe function in the form  $Y_T = (w_T - w_{27.07}) / (w_{90.19} - w_{27.07})$ . Between  $27.07^{\circ}$  and  $20.27^{\circ}$  a third calibration point at the normal boiling temperature of equilibrium hydrogen, deviations from  $Y_T$  can be made linear to within at most two millidegrees, provided the platinum is so pure that its  $\alpha$  exceeds 0.003925. However, these reproducibilities can be attained only provided the ratio  $\alpha/w_{4.2}$  (or possibly  $w_{20.27}/w_{90.19}$ ) of each calibrated thermometer falls within definite limits which can probably be realised for a majority of thermometers.

It is concluded that the SPS is sufficiently easily and accurately reproducible to justify its use for the extension of the ITS down to 20°K.

# TABLE OF CONTENTS.

	<u>Page.</u>
I. Introduction.	
(i) The Thermodynamic Temperature Scale.	1.
(ii) The International Temperature Scale.	2.
(iii) The Problem and the Program.	4.
II. Other Low Temperature Thermometers.	9.
III. Remarks on the Theory of Electrical Resistance in Metals.	
(i) General	12.
(ii) Matthiessen's and Nernst's Rules.	13.
(iii) Deviations from these Rules.	15.
(iv) A Theoretical Basis for negative Deviations.	22.
IV. A Review of Methods employed in Low Temperature Resistance Thermometry.	
(i) General.	24.
(ii) Curve Fitting Methods.	25.
(iii) Matthiessen's and Nernst's Rules.	27.
(iv) The Use of Tabulated Functions.	31.
V. Experimental.	
(i) The Resistance Thermometers.	35.
(ii) Resistance Measurements.	37.
(iii) The Cryostat and Associated Equipment.	37.
VI. Procedure, Results and Comments.	
(i) Low Temperatures.	47.
(ii) The Range 54°K to 90°K.	52.
(iii) Reliability of Results.	56.
(iv) Remarks on $dw/dT$ near 90°K.	58.
VII. The Correlation of $w$ - $T$ Data.	
(i) Some Characteristics of Platinum Thermometers.	61.
(ii) The Range 90° to 27°K.	67.
(iii) The Range 27° to 14°K.	70.
VIII. Conclusions.	78.
IX. Acknowledgments.	82.
Appendix I. The Para and Ortho Modifications of Hydrogen.	
(i) Introduction.	84.
(ii) Theory.	84.
(iii) Ortho-Para Transitions.	87.
(iv) The Measurement of the Para Content of Hydrogen.	90.
References.	95.

# LIST OF FIGURES.

(Titles abbreviated).

	<u>Page.</u>
1. $dR/dT$ versus $T$ .	7.
2. Electrical resistance in metals.	17.
3. Hoge and Brickwedde's results.	19.
4. Differences between various thermometers with $CH_6$ as standard.	20.
5. Los and Morrison's results.	21.
6. Differences between various thermometers with $L_6$ as standard.	25.
7. Van der Leeden's results.	29.
8. $(1/w)(dw/dT)$ versus $T$ .	34.
9. Construction of thermometers.	35.
10. Pumping lines associated with Cryostat.	42a.
11. Schematic diagram of cryostat operation.	42b.
12. The cryostat.	42c.
13. Intercomparisons between $R_{10}$ and $D_1$ .	50.
14. Intercomparisons of $CT_{15}$ with $CT_{18}$ and $R_{10}$ .	51a.
15. $dR/dT$ and $dw/dT$ versus $T$ for $CT_{15}$ .	54.
16. Differences between various thermometers with $CT_{15}$ as standard.	55b.
17. Differences between oxygen vapour pressure scales.	60.
18A. $\alpha$ versus $w$ at $90.19^\circ K$ .	61a.
18B. $\alpha$ versus $w$ at $4.2^\circ K$ .	61a.
19. $w$ at $20^\circ$ versus $w$ at $90^\circ K$ .	64.
20. Effect of purity on $dw/dT$	65.
21. $w$ at $54^\circ$ versus $w$ at $90^\circ K$ .	69.
22. $w$ at $15^\circ$ versus $w$ at $4.2^\circ K$ .	71a.

	<u>Page.</u>
23.     w at 20° versus w at 4.2°K.	71a.
24.     w at 54° versus w at 4.2°K.	71a.
A1.     Vapour pressures of oH <sub>2</sub> - pH <sub>2</sub> mixtures.	85.
A2.     pH <sub>2</sub> concentration in hydrogen.	87.
A3.     Calibration curve for Grilly cells.	93.
A4.     oH <sub>2</sub> - pH <sub>2</sub> conversion rates.	94.

# LIST OF TABLES.

(Titles abbreviated)

Page.

1.	Inversion temperature for $dR/dt$ of platinum.	5.
2.	Data on Intercomparisons between the helium gas thermometer and platinum resistance thermometers.	25a.
3.	Details of thermometers.	35a.
4.	Calibration of CT15 below $20^{\circ}\text{K}$ .	48a.
5.	Results for CT15, CT16 below $20^{\circ}\text{K}$ .	49a.
6.	Results for all NSL thermometers below $20^{\circ}\text{K}$ .	50a.
7.	$dP/dT$ for liquid oxygen.	52.
8.	Readings with CT15 between $54^{\circ}$ and $90^{\circ}\text{K}$ .	53.
9.	Smoothed results for CT15 between $55^{\circ}$ and $90^{\circ}\text{K}$ .	53a.
10.	Differences between CT15 and CT16 between $62^{\circ}$ and $90^{\circ}\text{K}$ .	55.
11.	Results for all NSL thermometers between $55^{\circ}$ and $90^{\circ}\text{K}$ .	55a.
12.	Cragoe Function to $20^{\circ}$ and to $30^{\circ}\text{K}$ compared.	66a.
13.	Cragoe Function to $54^{\circ}\text{K}$ .	67a.
14.	Cragoe Function to $27^{\circ}\text{K}$ .	68a.
A1.	Transition points of the hydrogen modifications.	89.

## I. INTRODUCTION.



(i) The Thermodynamic Temperature Scale.-- A temperature scale can be defined with reference to any property of a substance which is a function of the temperature. However, scales based on different thermometric properties or even on the same property of substances differing only in their degree of chemical purity or physical imperfections will in general differ by an amount which can be determined only by experiment (see e.g. Zemansky 1956, p.8). This effect will be the more pronounced the greater the impurity contribution to the overall magnitude of the property under investigation. For instance, the contribution by residual impurities to the resistance of highly pure platinum is less than 1 part in  $10^4$  near  $200^\circ\text{C}$  but between 1 and 2 parts in  $10^1$  near  $20^\circ\text{K}$  so that when the resistance of platinum is used as the thermometric property even very small differences in purity which are virtually insignificant near room temperature may have far from insignificant effects below  $20^\circ\text{K}$ .

It is then obvious that no thermometric substance offers a really satisfactory basis for the establishment of a temperature scale and once this was recognised, efforts were made to attack this problem in a different manner and to establish a temperature scale so selected that it would be independent of the thermometric substance. Such a scale is now known as the Thermodynamic Scale and all temperatures with only a few exceptions ultimately are numbered with reference to this scale.

For the region extending approximately from  $1^\circ$  to  $1400^\circ\text{K}$



the Thermodynamic Scale is established with reference to the properties of a so-called ideal gas, i.e. a gas satisfying the equation of state

$$\frac{P \cdot V}{T} = \text{constant}$$

where P is the pressure the gas exerts, V its volume and T its temperature on the Thermodynamic Scale. Although no real gas obeys this equation strictly, low boiling point elemental gases and especially nitrogen, hydrogen and helium deviate from it only by small and readily calculable amounts provided their pressures are sufficiently low. Hence, thermometers containing one of these gases as working substance (for temperatures much below 90°K this will have to be helium) can be used to obtain the Thermodynamic Scale (see e.g. Keyes 1941).

(ii) The International Temperature Scale.- Since gas thermometry is experimentally difficult and extremely cumbersome, there is no alternative in practice to the use of the more convenient thermometric properties of solid materials. To limit the consequences of their imperfections, instruments and methods of temperature measurements are rigidly circumscribed in an international agreement defining the so-called International Temperature Scale (ITS). With only a few amendments this scale has served as the temperature standard for the range from the normal boiling point of oxygen ( -182.97°C) upwards, since it was approved by the Seventh General Conference of Weights



and Measures in 1927. \*

The principal objectives aimed at in setting up the ITS are then twofold: (a) it is to be conveniently and accurately reproducible, thereby making it possible to specify temperatures to within much closer limits of accuracy than on the Thermodynamic Scale and (b) it is to agree with the Thermodynamic Scale as closely as possible in the state of available knowledge. A brief reference to the extent to which these objectives are realised is included in Part IV of the ITS 1948.

From 630° down to -183°C the International Temperature Scale is defined by two equations connecting the temperature with the resistance of a platinum wire. The first of these equations

$$R_t = R_0 (1 + At + Bt^2) \quad (1)$$

covers the range from 0° to 630° and is commonly used in the form given by Callendar

$$t - \theta = \delta \cdot \left( \frac{t}{100} \right) \cdot \left( \frac{t - 100}{100} \right) \quad (2)$$

where  $\theta$  is the platinum temperature and is defined by

---

\* The ITS was first published in Trav. Bur. Int. Poids Mes. Vol. 18, 1930, while the amended versions were published in the C.I.P.M. Proces-Verbaux des Seances, Vol. 21, 1948, and Vol. 24, 1954. An English translation of the 1948 version of the Scale was prepared by Mr. A. F. A. Harper and published in 1950 by the Division of Physics, National Standards Laboratory, Sydney.

$$\theta = (R_t - R_0) / \alpha R_0 \quad \text{and} \quad \alpha = (R_{100} - R_0) / 100R_0 .$$

The three constants ( $R_0$ ,  $A$ ,  $B$  or  $R_0$ ,  $\alpha$ ,  $\delta$ ) are determined by thermometer calibrations at the freezing and boiling points of water ( $0^\circ$  and  $100^\circ\text{C}$ ) and the boiling point of sulphur ( $444.6^\circ\text{C}$ ).

Below  $0^\circ\text{C}$ , continued agreement between the platinum scale and the Thermodynamic Scale can be secured only if equations (1) and (2) are modified as suggested by Van Dusen (1925) so that

$$R_t = R_0 \left[ 1 + At + Bt^2 + C (t-100) t^3 \right] \quad (3)$$

or

$$t - \theta = \delta \left( \frac{t}{100} \right) \left( \frac{t-100}{100} \right) + \beta \left( \frac{t}{100} \right)^3 \left( \frac{t-100}{100} \right) \quad (4)$$

This necessitates a four point calibration of the thermometer, the additional point being the boiling point of oxygen ( $-182.970^\circ\text{C}$ ).

It is further required that the constant  $\alpha$  which is generally the higher the purer the platinum wire (Van Dijk showed in 1952 that for ideally pure platinum it should be near 0.003928), must be at least 0.003910 (prior to 1948 this minimum was 0.00390), while  $\delta$  should be between 1.488 and 1.498 and  $0.5852 \delta - \beta$  should lie between 0.7656 and 0.7598.

(iii) The Problem and the Program.-- Although  $\delta$  is measured near  $440^\circ\text{C}$  (2) gives satisfactory results up to  $630^\circ\text{C}$  and even higher (Moser 1930, Pilipchouk 1954). Against this (4) ceases to be useful only a degree or two below the oxygen point (see Part IV, Section 3 of the ITS 1948) and this because  $d^2R/dt^2$  for platinum

changes sign in this temperature region (see Table 1). The temperature of the inversion point is not sharply defined and depends on the purity of the wire.

TABLE 1. Inversion Temperature for  $dR/dt$  of Platinum as a Function of its Purity.

Purity in terms of $\alpha$	Inversion Temperature (approx.)	Reference
0.003907	- 188° C	Henning & Otto 1936a
X 3917	X 186	Hoge & Brickwedde 1939
X 3926	X 185.5	Los & Morrison 1951

Nevertheless, platinum thermometry has been extensively employed below -183°C partly because equipment and techniques of measurements are readily available and known, and also because of the well established temperature stability of the platinum thermometer (Barber 1954, McLaren 1957) for stability obviously is a basic requirement for standard work. However, currently used calibration methods below 90°K are much more cumbersome and arbitrary than ITS calibration methods and there has long been a firm conviction that it would be a decided step forward if these latter methods could be extended. Numerous attempts have been made,

of course, to achieve this aim but so far none of the resulting recommendations has proved generally acceptable.

This problem is here re-investigated but from a more favourable position for firstly, the gas thermometric calibration of a thermometer made from very pure platinum is now available (Chambre Centrale des Mesures 1954) and secondly, it is now realised that the calibration of a platinum thermometer at the normal boiling point of helium ( $4.2^{\circ}\text{K}$ ) can give valuable information about its behaviour at and above liquid hydrogen temperatures.

The resistance - temperature ( $R-T$ ) relationship of platinum will be investigated near  $4^{\circ}\text{K}$  and from about  $14^{\circ}$  to  $90^{\circ}\text{K}$ . The  $14^{\circ}$  mark is generally chosen as the lower limit for platinum resistance thermometry, for very close to  $14^{\circ}$  (at  $13.81^{\circ}\text{K}$ ) ends a convenient calibration range based on the vapour pressure - temperature relationship of liquid equilibrium hydrogen (Woolley, Scott and Brickwedde 1948) and in any case below  $14^{\circ}\text{K}$  the value of  $dR/dT$  for platinum soon becomes so small (see Fig.1) that for the purpose of precision thermometry other thermometers should prove preferable (Scott 1955).

The account of the work begins with a brief reference to the claims of thermometers other than the platinum resistance thermometer to serve as temperature standard in the range of interest. Next some aspects of the conduction of electricity through metals are considered and this is followed by a review

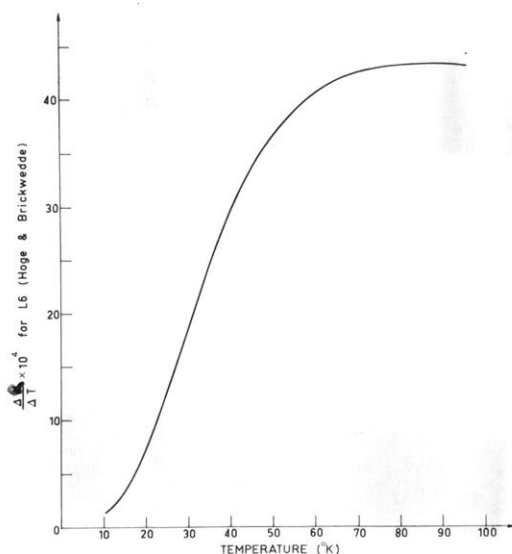


Figure 1.  $dR/dT$  for Platinum as a function of temperature.

of earlier attempts to discover a sufficiently simple and accurate relationship connecting the resistance of platinum with its temperature. The experimental part of the work consists of measurements on platinum resistors of differing purity in the ranges 14° to 20° and 54° to 90°K. Apparatus and procedure for these experiments are described and the results are listed and discussed. Finally, these results are correlated with as many of the published results as possible followed by recommendations concerning methods which may prove useful for the extension of the ITS below

90°K.

It must still be emphasised that the work here undertaken can be justified even without reference to the ITS for as long as the platinum thermometer remains, as it is at present, a widely used instrument for the measurement of temperatures below 90°K, the accumulation of further knowledge concerning the R - T relationship of platinum samples of differing purity must be of considerable importance to standard thermometry regardless of other considerations. Furthermore, such additional knowledge is also of interest to solid state physics.

## II. OTHER LOW TEMPERATURE THERMOMETERS.

While platinum thermometry was as yet relatively undeveloped, low temperature scales were established first by Glauque, Buffington and Schulze (1927) in California and then by Aston, Willihnganz, and Messerly (1935) in Pennsylvania by comparing copper-constantan thermocouples with the hydrogen and helium gas thermometer. The Scales extended to about 12°K and the optimum estimate of reproducibility in the liquid hydrogen range was  $\pm 0.05^\circ$  which in this region corresponds to an e.m.f. of less than 0.1  $\mu$ V in about 6000  $\mu$ V (see also Aston 1941). Thermocouples were then favoured on account of the small size and heat capacity of the junctions. Their relative advantage in this regard has been largely removed, however, since the development of the coiled coil platinum thermometer (Meyers 1932) enclosed in a platinum capsule (Southard and Milner 1933). This coil and the capsule are illustrated in Fig. 9 below.

The Pennsylvania Scale is now about to be replaced by a platinum resistance scale (Aston and Moessen 1953). On the other hand, Dauphinee, MacDonald and Pearson (1953) have developed copper v. dilute copper alloy thermocouples with promising properties for work in the region 2° to 30°K but their suitability for standard work remains to be established.



There have been, of course, numerous suggestions and experiments involving the use of various types of thermometers other than thermocouples. Some very early work was carried out on gold resistors (Cath, Onnes and Burgers 1917) but does not seem to have been revived other than at temperatures well below  $20^{\circ}\text{K}$ . After the last war, it was shown that resistors made from commercial copper wire can be useful and fairly accurate thermometers in cases where sudden temperature changes can be avoided (Dauphinee and Pearson 1954). Other resistance materials suggested as suitable between  $14^{\circ}$  and  $90^{\circ}\text{K}$  and claimed to be stable were germanium (Kunzler, Geballe and Hull 1957) and indium (White and Woods 1957)\*. A very different method has just been published by Benedek and Kushida (1957) based on the temperature dependence of the pure quadripole resonance frequency of the  $\text{Cl}^{35}$  nucleus in granular  $\text{K Cl O}_3$ .

All these methods remain to be thoroughly tried and tested especially in regard to long term stability in conditions commonly encountered by thermometers as well as the degree of uniformity in the thermal behaviour exhibited by different samples obtained in different laboratories. Taking the results as they stand, in no case is the overall measuring sensitivity significantly better than

---

\* White and Woods compared their indium thermometer with platinum thermometer T4 originally calibrated by Los and Morrison (1951). However, White and Woods presented the calibration data for T4 in a convenient form and added more low temperature data including the resistance at  $4.20\text{K}$ . Therefore, White and Wood's paper will be referred to throughout this thesis whenever reference is made to T4.



that obtainable with platinum resistors while the Benedek and Kushida thermometer suffers from the drawback of requiring highly specialised measuring instruments and techniques. Finally, the serious handicap to which low temperature platinum thermometry is still subject, namely the absence of a sufficiently simple and at the same time accurate calibration procedure is shared by all other thermometers.

It can be concluded, therefore, that as yet no other instruments available are likely to replace platinum resistors as standard thermometers in the range  $14^{\circ}$  to  $90^{\circ}\text{K}$  and it is with platinum resistance thermometry only that the work embodied in this thesis has been concerned.

### III. REMARKS ON THE THEORY OF ELECTRICAL RESISTANCE IN METALS AND MATTHIESSEN'S RULE.

(i) General.- The resistance-temperature (R-T) relationships (1 - 4) employed in platinum thermometry above 90°K were obtained by empirical methods when theories about the transport of electricity in metals were still in their infancy. Although these theories have been advanced considerably, it has still not been possible to develop a reliable theoretical expression for the observed variations of resistance with temperature even in monovalent metals (MacDonald 1956) and much less so for platinum which belongs to the transition group although theoretical arguments can be adduced (Baber 1937, Pines 1956) to explain results by De Haas and De Boer (1933), Sudovtsov and Semenenko (1956) and White and Woods (1957a) near and below 10°K where  $T \propto \rho^2$ . Unfortunately,  $d\rho/dT$  is then also so small that platinum thermometers are no longer really suitable for precision thermometry (see Fig.1).

On the other hand, the mechanism producing electrical resistance in metals is well understood at least in general terms. Briefly, such resistance is due to disturbances of the regular periodicity of the crystal lattice caused by (a) thermal vibrations or (b) chemical or physical imperfections. These disturbances scatter the electrons and so tend to reduce the current thereby balancing the tendency of the electric field to increase the current, and maintaining a steady state of finite conductivity.

By assuming that scattering due to thermal vibrations and imperfections respectively, are independent of one another at least to a first approximation, it is at once possible to account for the results of Matthiessen and Vogt (1864) who had shown that the increase in the resistance of a metal due to small quantities of added impurities forming solid solutions is in general independent of temperature.

(ii) Matthiessen's and Nernst's Rules.- Matthiessen's rule (M.R.) can then be expressed by the following two equations

$$\rho_T = \rho_i + \rho_r \quad (5)$$

$$\frac{d}{dT} (\rho_T) = \frac{d}{dT} (\rho_i) \quad (6)$$

Here  $\rho_T$  is the observed resistivity at some temperature  $T$ ,  $\rho_i$  its component due to scattering process (a) and  $\rho_r$  due to (b). The former, being the only one depending on temperature, is often referred to as "Ideal" resistivity, the latter as residual resistivity for as  $T \rightarrow 0$ ,  $\rho_i \rightarrow 0$  and, therefore,  $\rho_0 = \rho_r$ .

In many cases it is not important to measure absolute resistivity but only changes relative to the resistivity at some chosen temperature, generally  $0^\circ\text{C}$ . Thus applying (5) to the difference between the resistivities of two samples  $\rho$  and  $\rho'$  respectively, both at temperature  $T$  ( $\rho_i$  then being the same for each).

$$\rho'_T - \rho_T = \rho'_r - \rho_r = b \text{ (say)}$$

where  $b$  is taken as constant for any given pair of resistors.

Consequently,

$$\rho_T = \rho'_T - b$$

and if  $T = 0^\circ\text{C} = 273^\circ\text{K}$

$$\rho_{273} = \rho'_{273} - b$$

so that

$$\frac{\rho_T}{\rho_{273}} = w_T = \frac{\rho'_T - b}{\rho'_{273} - b}$$

On dividing the r.h.s. by  $\rho'_{273}$  and putting  $b/\rho'_{273} = n$

$$w_T = \frac{w'_T - n}{1 - n} \quad (7)$$

Equation (7) was first suggested by Nernst (1911) and is generally known as Nernst's Rule.

Nernst's Rule can, of course, be used also with reference to an ideal resistor (see e.g. Meissner 1935) for it follows again from (5) that

$$\frac{(\rho_i)_T}{(\rho_i)_{273}} = (w_i)_T = \frac{\rho_T - \rho_r}{\rho_{273} - \rho_r}$$

and on dividing the r.h.s. by  $\rho_{273}$  and setting  $\rho_r/\rho_{273} = z$

$$(w_i)_T = \frac{w_T - z}{1 - z} \quad (8)$$

Consequently, at any temperature  $T$  and for any number of resistors  $w_1, w_2, \dots, w_j$

$$\frac{w_j - z_j}{1 - z_j} = \text{constant} \quad (9)$$

It should be noted here that on making the reasonable assumption that volume changes are negligible

$$\frac{\rho}{\rho_{273}} = w = \frac{R}{R_{273}} \quad (10)$$

and this substitution is in fact generally used in resistance thermometry and will also be used in the present work.

(iii) Deviations from these Rules.- Tests on platinum wires (and also, of course, with other metals, see e.g. Grinneisen 1933) have shown all along large deviations from these equations (see Section IV below) but notwithstanding this M.R. was believed to be well founded for a considerable time, the change of ideas coming about mainly as the result of the work of Sondheimer and Wilson.

In monovalent metals conduction occurs only in the  $S$  band of electrons and its resistivity was envisaged as a series combination of the two resistivities  $\rho_i$  and  $\rho_r$ . It was then shown by Sondheimer (1950) that  $\rho_i$  and  $\rho_r$  do not simply combine additively but that always  $\rho > \rho_i + \rho_r$ , the inequality becoming greatest when  $\rho_i$  and  $\rho_r$  are comparable in magnitude. Consequently equation (1) becomes

$$\rho = \rho_i + \rho_r + \Delta \quad (11)$$

where  $\Delta$  is always positive, depends on temperature and can be considered as a deviation term from M.R.

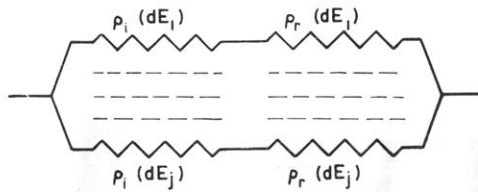
The reasons for these deviations lie in the nature of the solution to the Bloch integral equation (Bloch 1930) governing the electron distribution. It may be pictured as follows; electrons of different energies contribute additively to the conductivity, the main contribution coming from those within a few  $kT$  ( $k$  being Boltzmann's constant) above and below the Fermi energy. However, the resistance due to the scattering by lattice waves experienced by electrons in each energy layer varies with energy so that the overall resistivity can be represented by a network analogous to that shown in Fig. 2a where the branches refer to successive energy layers ( $dE_1, dE_2, \dots, dE_j$ ). Clearly for such a network M.R. would hold only if  $\rho_i(dE_j)$  and  $\rho_r(dE_j)$  were in constant proportion. In general, there will be a deviation ( $\Delta$ ) which must be determined by experiment for although Sondheimer succeeded in calculating  $\Delta$  as a function of  $T$  and  $\sigma_r$ , his calculated values were in all cases smaller than the observed values (Wilson 1953, p.311, Krantz and Schultz 1957).

In transition metals such as platinum conduction occurs both in the s and d bands which can be represented by two pairs of resistors in parallel (see Fig.2b) namely

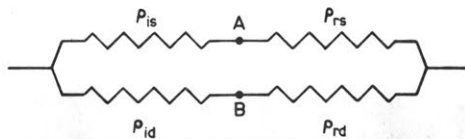
$$\rho_s = \rho_{is} + \rho_{rs} = 1/\sigma_s$$

$$\rho_d = \rho_{id} + \rho_{rd} = 1/\sigma_d$$

where  $\sigma_s$  and  $\sigma_d$  are the respective conductivities, the total



(a) RESISTANCE TO ELECTRON FLOW IN THE VARIOUS ENERGY LAYERS ( $dE_i, \dots, dE_j$ ) OF THE S-BAND.



(b) ELECTRICAL RESISTANCE IN TRANSITION METALS (TWO BAND MODEL) AFTER SONDHEIMER & WILSON (1947). A DIAGRAM BASED ON THE VALIDITY OF MATTHIESSEN'S RULE WOULD SHOW POINTS A, B CONNECTED.

Figure 2. Electrical Resistance in Metals.

conductivity  $\sigma$  being given by

$$\sigma = \sigma_s + \sigma_d$$

On the other hand, for M.R. to be valid the analogous circuit would require a connection from point A to B for then

$$\rho = \frac{\rho_{is} \cdot \rho_{id}}{\rho_{is} + \rho_{id}} + \frac{\rho_{rs} \cdot \rho_{rd}}{\rho_{rs} + \rho_{rd}}$$

Since the total resistance of the network as shown in Figure 2b cannot be smaller than that when points A, B are connected, deviations from M.R. must again be positive and this even before considering the mechanism discussed above (Fig.2a), which must



increase  $\Delta$  still further. It is then evident that M.R. cannot hold for the network shown in Fig. 2b and this even in cases where it holds for each branch separately for it is not possible to express  $\rho$  as the sum of  $\rho_i$  and  $\rho_r$  such that  $\rho_i$  depends only on  $\rho_{is}$  and  $\rho_{id}$  and  $\rho_r$  depends only on  $\rho_{rs}$  and  $\rho_{rd}$  (Sondheimer and Wilson 1947).

Later Wilson (1953, p.312) pointed out that for low temperatures the deviation term  $\Delta$  can be expressed at least qualitatively by

$$\Delta = \frac{a\rho_i\rho_r}{b\rho_i + c\rho_r} \quad (12)$$

where  $a$ ,  $b$ ,  $c$  are quantities of the order of unity and possibly temperature dependent. Clearly, for  $T$  small enough so that  $b\rho_i \ll c\rho_r$  equation 12 reduces to  $\Delta \approx \rho_i$  while for  $\rho_i \gg \rho_r$   $\Delta \sim \rho_r$  i.e. as the temperature rises  $\Delta$  approaches an upper limit so that M.R. is then apparently satisfied. For highly pure platinum ( $\alpha \sim 0.003925$ ) this should occur between  $20^\circ$  and  $25^\circ\text{K}$  but for platinum having  $\alpha \sim 0.00391$  it should occur only above about  $50^\circ\text{K}$ . Consequently, the difference between the resistivities of a highly and less pure sample respectively should keep increasing for about two thirds of the range up to  $90^\circ\text{K}$ .

If their standard L6 were accepted as being closely similar to an ideal resistor, Hoge and Brickwedde's (1939) results (see Fig.3) would give some support to such a theory (Schultz 1957). However, the comparison between the  $w - T$



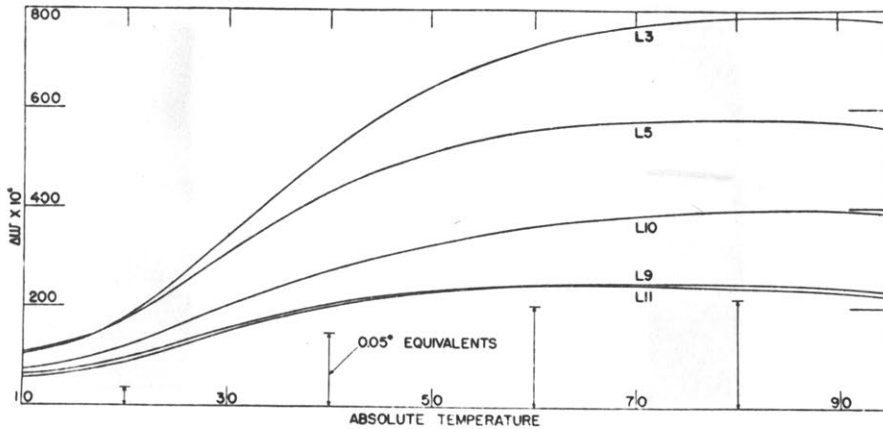


Figure 3. Comparisons between w-T Scales of Thermometers calibrated by Hoge and Brickwedde ( $\Delta W = W_{no} - W_{L6}$ )

scales of several thermometers shown in Fig. 4 (see also Fig. 16 below) clearly indicates that when referred to a resistor having  $\alpha > 0.003925$  and so likely to be more nearly representative of an "ideal" resistor than L6 which has  $\alpha \sim 0.003917$  will reach a maximum which can occur anywhere between  $30^\circ$  and  $60^\circ K$ , it will then decrease and may even become negative in some cases. Hoge and Brickwedde's curves (Fig. 3) represent special cases of resistors having  $\alpha$  not very high purity intermediate between those shown by curves B and C (Fig. 4) respectively. The resistors used by Los and Morrison (1951) represent another special case, all of them being highly pure

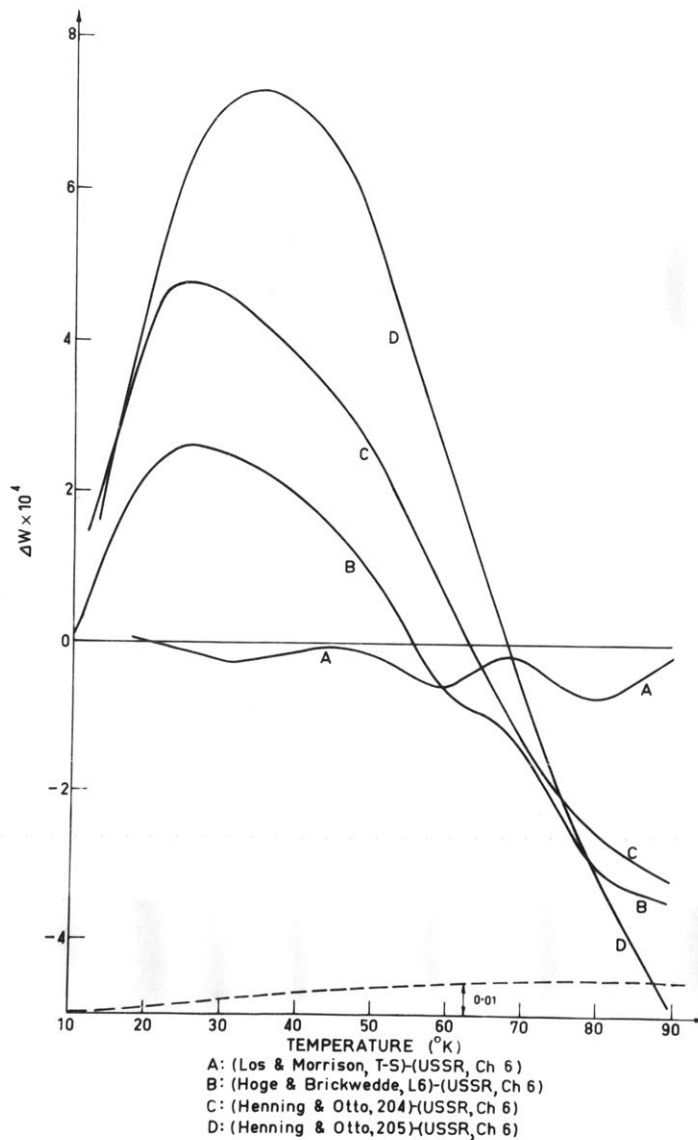


Figure 4.  $w - T$  Scales for various Thermometers referred to Ch6 as Standard.

(To achieve clearer representation, the differences represent not simply  $w - w_{\text{ch6}}$  but  $(w - w_r) - (w - w_r)_{\text{ch6}}$ . Values were obtained by extrapolation)

of  $w_r$

( $0.0039255 > \Delta > 0.0039260$ ) and there  $\Delta$  is in fact negative throughout (see Fig.5). All  $\Delta$  values are, of course, also very small and their variations with temperature were found to be sufficiently regular (when referred to the same standard scale) for Los and Morrison to succeed in representing the  $\Delta - T$  relation by a sine function. All this suggests that groups of platinum wires are most likely to fit a common  $R - T$  relationship when their impurity contents fall within sufficiently narrow limits but it does not seem necessary that it be extremely low. These points will be considered in detail in Section VII below.

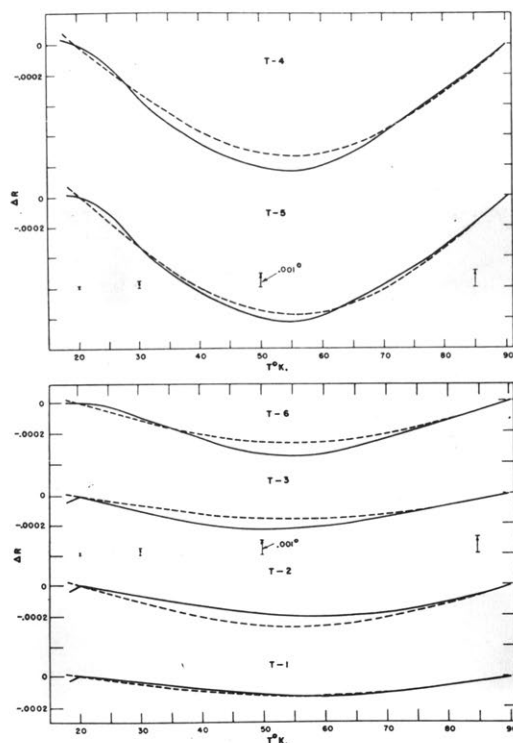


FIG. 1. The relationship between  $\Delta R$  and temperature for the six thermometers.  
 —  $\Delta R$  determined from the intercomparison data.  
 - - -  $\Delta R$  calculated from Equation (IV).

Figure 5. Differences from their standard scale for six thermometers calibrated by Los & Morrison.

—  $R$  from intercomparison data  
 - - -  $R$  from interpolation formula

(iv) **A Theoretical Basis for Negative Deviations.**-- The results shown in Fig. 4 evidently do not fit Sondheimer and Wilson's theory and new assumptions will have to be made and investigated concerning possible causes for the observed decrease in  $\Delta$  . It had been assumed in all the preceding arguments that imperfections do not affect the temperature dependent scattering of electrons by lattice waves which is the cause of  $\rho_i$  but in fact imperfections must be expected to generally alter the band structure by altering the number of electrons in each band and thus alter the effective number of electrons and their scattering probabilities, an effect which will be particularly pronounced when the imperfections are impurities of different valency from the parent metal (Mott and Jones 1936, p.289).

For monovalent metals the resulting effect on their conducting properties may not be appreciable since their band structure may be approximated by a gas of free electrons. In transition metals conductivity is due mainly to s band electrons which are scattered partly within the s - band (s-s transitions) and partly into the d - band (s - d transitions), the latter process being the predominant contributor to the electrical resistance at low temperatures (Kemp et al. 1955). The structure of the d - band is usually complicated (see e.g. Raynor 1952) and it is known from measurements of the electronic specific heat (Rayne 1957) that small concentrations of impurities can change

the density of states quite appreciably by a small change in the number of electrons in this band. If the density of states is changed, it is likely that the transition probability for s - d transitions is also changed and with it  $\rho_{is}$ . Depending on the nature and the amount of the contamination  $\rho_{is}$  may be increased or decreased leading either to positive or negative deviations from M.R. This effect could well be more important than the Sondheimer-Wilson mechanism because the conductivity of the d - band is likely to be very small (Klemens, pers. comm.) so that the overall resistance of the circuit shown in Fig. 2b would be very nearly that of the s branch only and deviations due to the d branch would be small.

#### IV. A REVIEW OF METHODS EMPLOYED IN LOW TEMPERATURE

##### RESISTANCE THERMOMETRY.

(i) General.- Use of the electrical resistance of metals at low temperatures as a thermometric property must take account of the fact that this low temperature resistance is very sensitive to all changes in the characteristic parameters of metals (MacDonald 1956, p.137). This fact, which has been fully appreciated only relatively recently, largely explains the failure of successive investigations with platinum resistors to produce consistent results comparable to those obtainable between  $90^{\circ}$  and  $273^{\circ}\text{K}$ , where platinum thermometers satisfying present ITS requirements can be relied upon to yield the same temperature scale to well within  $0.01^{\circ}$  (Hoge and Brickwedde 1942, Stimson 1952).

Not surprisingly the most striking inconsistencies appeared during the earlier investigations (see e.g. Onnes and Tuyn 1924). Since 1927 and partly due to the stimulus given to platinum thermometry by the ITS there have been substantial improvements (especially since the war) in the equipment and techniques of measurements (Stimson 1955) and in the quality of commercially available platinum wire; but notwithstanding these factors, there have been only limited successes in the low temperature field.

In the following account the whole subject is discussed under three headings, namely, the fitting of experimental results

to selected polynomials in sub-section ii, the use of Matthiessen's and Nernst's Rules and of expressions of the general type  $R_1 = f(R_2)$  in sub-section iii, and, finally, the use of tabulated functions in sub-section iv. All this work was, of course, based on direct comparisons between platinum resistance thermometers and the helium gas thermometer. A brief summary of such data published since 1924 is given in Table 2. Some of these groups of measurements were intercompared graphically by Hoge and Brickwedde using their thermometer L6 as standard. This inter-comparison is reproduced in Fig. 6.

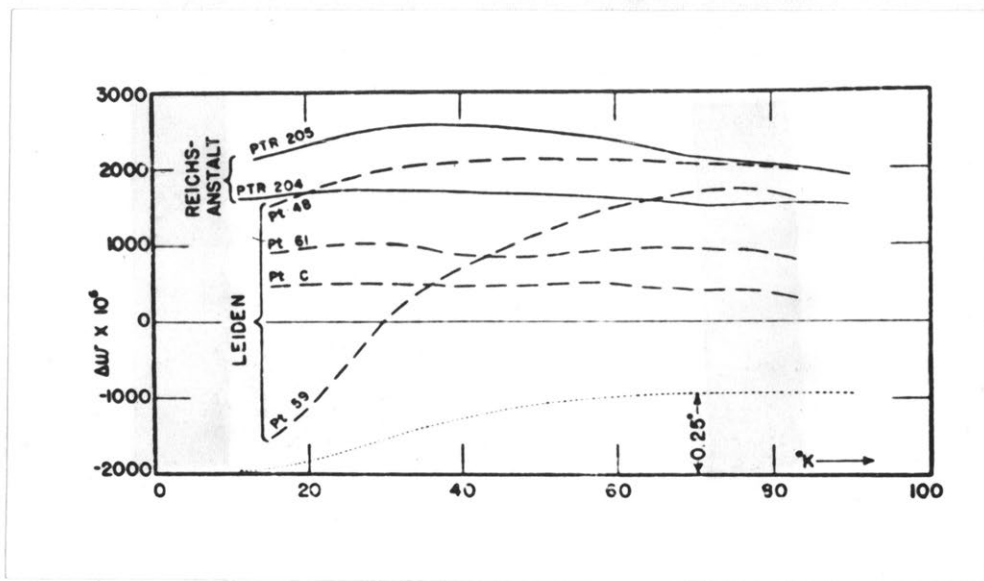


Figure 6.  $w - T$  scales for various Thermometers referred to L6 as standard ( $\Delta w = w_{no} - w_{L6}$ )

(ii) Curve Fitting Methods.-- Following the procedure used successfully by Callendar for the higher temperatures, attempts were made at Leiden (Onnes and Clay 1906, Keesom and Bijl 1936) to fit the results obtained by comparisons with the helium gas



Table 2 Data on Intercomparisons between the Helium Gas Thermometers and Platinum Resistance Thermometers.

Reference	Range and Intervals	Numbers of Thermometers and Remarks	Purity of Platinum in terms of $\alpha$
Onnes and Tuyn, 1924.	-270° to -80°C in 1°	1915 - 23' over entire range. Several other instruments over various parts of this range.	for 23' < 0.0039
Henning and Otto, 1932.	11° to 90°K in 1°	PTR 204	~ 0.00391
Southard and Milner, 1933.	14° to 90°K in 1°	K 2 K $\bar{V}$ Later work at the NBS showed that in the range 30° to 45°K errors may have reached 0.05°.	0.003917 0.003912
Keesom and Bijl, 1936.	4.2°K -258° to -190°C in 2° -182.98°C	Pt 48, Pt 59, Pt 61 Pt 6. The platinum for Pt 59 was obtained by thermal decomposition of Pt 60 61 <sub>2</sub>	respectively 0.003875 3905 3913 3915
Henning and Otto, 1936 <sub>a</sub> .	13° to 90°K in 1°	PTR 205	0.003907
Hoge and Brickwedde, 1939.	10° to 95°K in 1°	L 3, L 5, L 6, L 9, L 10, L 11; L 6 being used as standard	from 0.003912 to 0.003917
Chambre Centrale des Mesures, 1954.	10° to 95°K in 1°	ION Ch 6	~ 0.003925



thermometer to expressions of the general form  $T = f(R)$  or  $R = f(T)$ , the functions being polynomials with up to five constants to be determined at specified calibration points (generally the triple and boiling points of hydrogen and oxygen and the boiling point of nitrogen which to the nearest degree Kelvin have the respective values 14, 20, 54, 90 and 78). Though a great deal of trouble was taken over these attempts, no expression applicable to all tested thermometers could be derived (Keesom and Bijl 1936).

Henning and Otto (1932a) set up a five constant expression based on the Grueneisen (1930) theory of electrical resistance in metals. Notwithstanding this quasi theoretical basis, their success was rather limited, the formula representing the scales of several thermometers, including one calibrated by Southard and Milner (1933) at the N.B.S. to only within about  $0.1^{\circ}$  (Henning and Otto 1936b).

None of the instruments used in these comparisons had  $\alpha > 0.003917$ , which was then considered a very satisfactory value, and many had  $\alpha < 0.00391$ . It is an open question whether either purer platinum or expressions with more than five constants could have improved the results significantly though it is clear to-day that use of more uniformly pure platinum would have produced better agreement (see III,iii). Regarding additional constants, even five of these require an inconveniently large number of fixed point calibrations so that formulae with more than five

constants must be considered as highly impractical, apart from the fact that such multiconstant expressions are in any case undesirable on statistical grounds (see e.g. Jeffreys 1937, p.40). The polynomial approach to low temperature resistance thermometry is unlikely therefore to be revived.

(iii) Matthiessen's and Nernst's Rules.- Matthiessen's Rule (M.R.) was first applied by Henning (1913) in the form given it by Nernst (see equation 7 above). Thereby the resistance of an element can be expressed in terms of some selected standard rather than in terms of the somewhat intangible "ideal" resistance and, more important, provided the standard and test resistors all show similar deviations from M.R., the Nernst function, being the quotient of two differences, remains relatively unaffected. Finding that the Nernst Rule (N.R.) nevertheless was inadequate, Henning supplemented this expression by adding a quadratic correction term but even this brought only a very limited measure of agreement and further extensive tests in Leiden confirmed the earlier failures (Cath et al. 1917).

In 1928 Henning suggested yet another modification of M.R. which was tested by Southard and Milner (1933) who found that when used in conjunction with their  $w - T$  table temperatures in the range  $20^{\circ}$  to  $90^{\circ}$  should be calculable to within  $0.05^{\circ}$  provided the unknown resistor has similar characteristics to their standard K2. <sup>‡</sup>

---

<sup>‡</sup> Dr. Southard reported that their scale was subject to a computational error (see Hoge and Brickwedde 1939).

Van der Leeden (1941, p.153) made measurements on five resistors of widely differing purity, only one of them, however, was pure enough to satisfy present ITS requirements. Although his calibration range extended from  $14^{\circ}$  to  $20.5^{\circ}$  only, his contribution was important for two reasons. Firstly, he determined the relative residual resistance ( $z$ ) in each case (from measurements near  $4^{\circ}\text{K}$ ) and secondly he appears to have been the first to deduce deviations from M.R. as a function of temperature.

Van der Leeden modified (8) to

$$w_1 = \frac{w_T - (1+A)z}{1 - z} \quad (13)$$

where  $A$  is a constant depending on temperature only. The value of  $A$  at each temperature was obtained by plotting  $z$  versus  $w_1$  as defined by (8) for each one of his five resistors (see Fig. 7). With  $A$  known (13) could be used to generate five corresponding  $w_1$  scales. The agreement between these scales was unsatisfactory, however, at least for precision work and this is apparent from Fig. 7 although not clearly since the data was plotted on a rather constricted scale (the arrows superimposed on the curves represent temperature intervals of  $0.5^{\circ}$ ). One reason for the deviations is almost certainly found in the great variations in the physical and chemical purity of the platinum wires, particularly since only two of them (Pt1 and Pt3) were properly annealed.

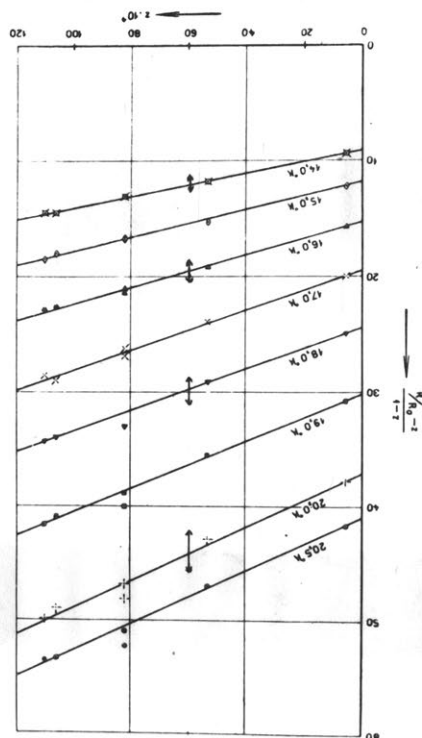


Figure 7. Deviations from M.R. as function of temperature after van der Leeden.

The last investigation to fall substantially into this category is that published by Hoge (1950). He found that the resistances of seven N.B.S. calibrated thermometers having  $\alpha > 0.003920$  could be expressed as a linear function of any selected two of that group so that at any given temperature

$$(R_1)_T = A (R_2)_T + B (R_3)_T + C \quad (14)$$

where  $R_2, R_3$  refer to two instruments for which  $R$  is known as a function of  $T$  while  $A, B, C$  are calibration constants belonging to  $R_1$  and determined near  $14^\circ, 20^\circ$  and  $90^\circ K$  respectively. Equations of the type (14) were found to predict

$R_1$  for the entire range  $14^{\circ}$  to  $90^{\circ}$ , errors being no greater than the equivalent of a few millidegree.

The Hoge and van der Leeden methods are really very similar, the difference being mainly that van der Leeden used a single standard scale and a table of deviations from this scale beginning at  $4.2^{\circ}\text{K}$  while Hoge used two standard scales which allowed him to do without the residual resistance. Both methods were based on the assumption that  $R$  depends essentially only on the total quantity of impurities (as measured by the residual resistance) but is relatively independent of their nature. Such an assumption can hardly be supported by theory (see III, iv) and moreover, it is contradicted by several measured results among the most drastic cases being the Leiden thermometer Pt59 (Fig.6) and thermometer R10 used during the present work (Fig.16 below). Nevertheless, this assumption is at least effectively true for some groups of thermometers such as those tested by Hoge and this fact is certainly significant (see III, iii).

It is still necessary to mention a paper by Van Dijk (1952) who analysed the expressions put forward by v.d. Leeden, Hoge, and Los and Morrison (for the latter see sub-section iv below) and showed that they could all be considered as special cases of a more general interpolation formula based on

$$w_T = w_1 + f(w_1, z, B) \quad (15)$$

where  $B$  represents two constants related to van der Leeden's  $A$ .

Van Dijk gave no examples, however, showing how far such a formula

could be successful and this presumably because published R - T tables did not include sufficient data for the evaluation of his constants.

(iv) The Use of Tabulated Functions.- Continued failures to establish precise interpolation formulae for platinum between 20° and 90°K led the U.S. National Bureau of Standards to define a Provisional Temperature Scale (PTS) based on a selected standard thermometer (Hoge and Brickwedde 1939). This instrument (L6) was calibrated against a helium gas thermometer together with five other platinum resistors. The results obtained for L6 were published in the form of a table giving  $w_{L6}$  at 1° intervals from 10° to 95°K together with suitable expressions for interpolation so that any temperature could be deduced from the corresponding resistance to a much higher accuracy (within a few millidegree) than had theretofore been possible. The results for the other five instruments were presented in the form of difference curves (see Fig. 3 above). The just mentioned order of accuracy is, of course, restricted to measurements on the PTS. Agreement with the Thermodynamic Scale was not thought to be better than  $\pm 0.02^\circ$ . The PTS fulfilled a long-standing demand for a reliable and continuous scale in a temperature range where for reasons implicit in the account given in (ii) and (iii) above, the need for such a scale was particularly pressing.

More recently, another w - T table has been published by the Chambre Centrale des Mesures, U.R.S.S. (1954) based on a thermometer (ION Ch6) of considerably higher purity than L6



(see Table 2). The resistance measurements were carried out with still greater accuracy than those of Hoge and Brickwedde but the accuracy on the Thermodynamic Scale was not claimed to be greater than  $\pm 0.02^{\circ}$ . Referring to Fig. 4, the slight irregularities shown by the differences between L6 and Ch6 above about  $60^{\circ}$  are almost certainly due mainly to differences in the gas thermometry scales rather than to differences in the behaviour of the respective platinum wires. Hoge and Brickwedde had come to a similar conclusion when commenting on the difference curves shown in Fig. 6 above. It may still be noted that the irregularities of Curve A, not surprisingly, can be correlated with those of curve B since Los and Morrison's scale was based on the PTS (see below).

By 1947, about 50 thermometers had been calibrated on the PTS. It was then suggested by Cragoe (see Stull 1949) to use these results for the testing of the expression

$$Y_T = \frac{R_T - R_1}{R_2 - R_1} \quad (16)$$

which he expected to be a function of the temperature only ( $R_1$ ,  $R_2$  being constants for each thermometer to be determined at suitable fixed points). Cragoe chose this expression because it corresponded to Callendar's platinum temperature ( $\theta$  in equation 2). It is, of course, also a particular form of the Nernst Rule equation (7) which is at once evident on dividing each term of the r.h.s. by  $R_2$ . Hoge found that with calibrations at the boiling and triple points of oxygen  $90.19^{\circ}$  and  $54.36^{\circ}$ )  $Y$  was



indeed constant to within a few millidegree but when  $R_1$  was determined at the boiling point of hydrogen,  $Y$  varied by more than  $0.05^\circ$ .

Later, Los and Morrison (1951) using only highly pure thermometers ( $\alpha > 0.0039255$ ) found that for a lower limit of  $54^\circ$  the Cragoe function reproduced a  $Y_T$  scale as calculated from the  $w - T$  table of their standard thermometer TS (originally calibrated on the ITS) with a maximum error of  $0.001^\circ$ , but its use down to  $20^\circ$  resulted in errors which nearly reached  $0.01^\circ$  in some cases (see Fig.5). These results were probably responsible for the abandoning of an N.B.S. proposal (Proces Verbaux 1948) to use the Cragoe function for the extension of the ITS to  $20^\circ\text{K}$ .

To demonstrate why (16) was found to be reasonably successful down to about  $54^\circ$ , it is only necessary to put  $R_1/R_{273} = a$ ,  $(R_2 - R_1)/R_{273} = b$ , and as usual  $R/R_{273} = w$ . It then follows from (16) that

$$\frac{w - a}{b} = \frac{w^l - a^l}{b^l}$$

and, therefore,  $w \propto w^l$  and also

$$\frac{1}{w} \frac{dw}{dT} \propto \frac{1}{w^l} \frac{dw^l}{dT} \quad (17)$$

It is evident from Fig. 8 that (17) should hold fairly closely down to the neighbourhood of  $30^\circ\text{K}$  notwithstanding considerable differences in impurity content. Below this,

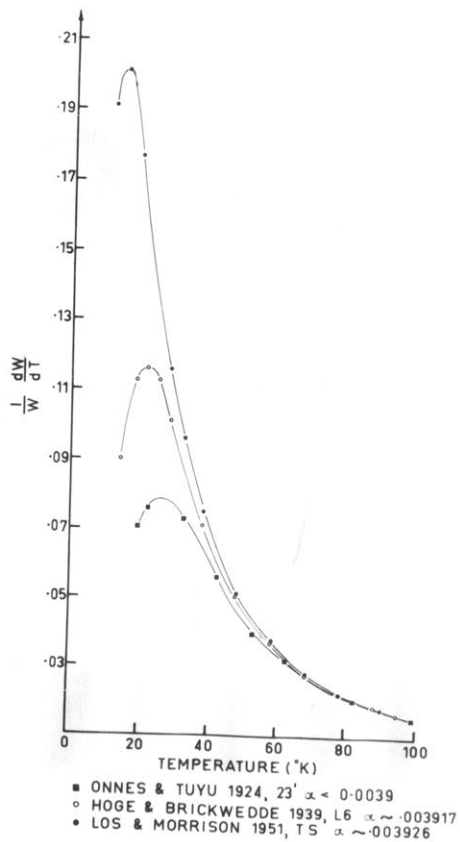


Figure 8. The Temperature Co-efficient of Platinum as a Function of Temperature.

however, the proportionality relations break down unless impurity contents are very similar indeed so that (16) can no longer be expected to hold. The exact limits within which (16) can be expected to be valid will be reconsidered in VII below.

## V. EXPERIMENTAL.

(i) The Resistance Thermometers.-- Measurements were made on five thermometers details of which are given in Table 3. All were made in accordance with Meyers (1932) method and enclosed in capsules as described in 1933 by Southard and Milner (see Fig. 9).

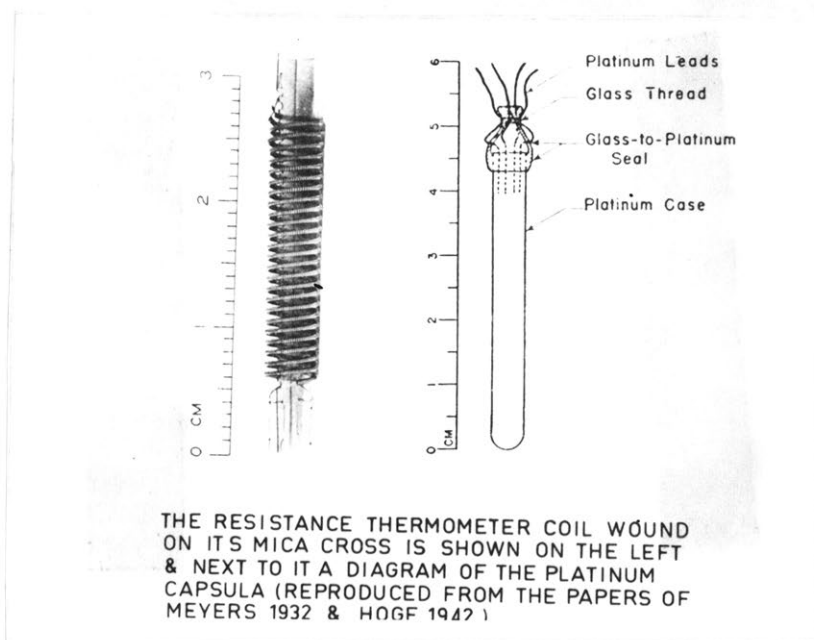


Figure 9. Construction of Resistance Thermometers.

Because some sections of the coils of R10 and D1 did not lie entirely within the serrations of their respective mica crosses, these coils had to be enclosed into soda glass capsules to avoid short circuits. Fortunately, it proved possible to make the glass capsules of substantially the same dimensions as the platinum capsules.

Coils CT15 and CT16 were made in 1954 from the same reel of wire and calibrated prior to sealing them into the platinum

Table 3

## Details of Resistance Thermometers

No.	Platinum	Capsula Material	$R_{0^{\circ}\text{C}}$ ohms	$\frac{R_{4.2^{\circ}\text{K}}}{R_{0^{\circ}\text{C}}}$	$\alpha \times 10^2$	$\delta$	$\beta$
CT 15	S. Cohn New York	platinum	22.8289	.000639 <sub>0</sub>	.39257 <sub>7</sub>	1.494 <sub>2</sub>	0.1088
CT 16	S. Cohn New York	platinum	22.6054	.000650 <sub>0</sub>	.39256 <sub>2</sub>	1.493 <sub>7</sub>	0.1088
CT 18	Johnson Matthey Ltd.	platinum	23.2602	.000890 <sub>0</sub>	.39237 <sub>0</sub>	1.496	0.109 <sub>3</sub>
R 10	Johnson Matthey Ltd.	soda glass	23.5680	.001609 <sub>3</sub>	.39113 <sub>0</sub>	1.498 <sub>4</sub>	0.1121
D 1	Johnson Matthey Ltd.	soda glass	25.7745	.004397 <sub>1</sub>	.38976 <sub>0</sub>	1.501 <sub>7</sub>	0.1181

capsules. Constants  $R_0$ ,  $\alpha$  and, of course,  $\beta$  were re-measured during the present work but not  $\delta$  since capsules cannot be safely heated above about 150°C.

Coil CT18 was made as part of the present project, the wire being taken from a sealed reel marked "thermopure". After annealing it for 10 hours at 480°C, it was at once sealed into its platinum capsule and  $\delta$  was determined by a comparison with CT15 at 50°C. This gave  $1.496 \pm 0.004$ , the relatively large margin of error being due mainly to the uncertainty in  $\alpha_{CT18}$ . Using the calibration results near 90°K and  $\delta = 1.496$  gives  $\beta = 0.1093$  and  $0.5882 \delta - \beta = 0.7661$  which is actually just a little high for ITS requirements.

Coil R10 had been made and calibrated in 1952 and since then used extensively for routine calibration work. It was re-calibrated prior to being sealed into its capsule and  $R_0$  was then checked again. Both  $R_0$  and  $\alpha$  had remained virtually stable since the original calibration.

Coil D1 was made at the Defence Standards Laboratories, Maribyrnong, but not sealed until its arrival at the N.S.L. Its  $\alpha$  was then found to be well below ITS requirements. The wire may have been contaminated at some stage prior to the sealing into its glass capsule. On the other hand, it had been noted on other occasions that unless requested to be sent in sealed containers and certified as "thermopure", Johnson and Matthey wire often had  $\alpha < 0.03910$ .

(ii) Resistance Measurements.- These were made with a Mueller Bridge (see e.g. Eppley 1932) the coils of which are periodically calibrated against standard resistors maintained by the Division of Electro-Technology in the N.S.L. The bridge readings can be considered as accurate to within a few parts in  $10^6$ .

(iii) The Cryostat and Associated Equipment.- Preliminary work on the extension of the ITS to the liquid hydrogen range had been initiated at the N.S.L. before this writer's arrival during August 1956. A cryostat had been designed by Mr. W. R. G. Kemp and had been assembled together with most of the necessary auxiliary equipment. This assembly will now be described and for this purpose will be divided into the cryostat proper, i.e. the section in which the low temperature is established and maintained, and three pumping lines comprising the associated apparatus. Two of the pumping lines are shown in Fig. 10, the third in Fig. 11, and a schematic diagram of the cryostat in Fig. 12 (The tubes leading into the cryostat are marked, with the same letters A, B.....G in each diagram.).

a. The Pumping lines. From the rotary and mercury diffusion pumps (1 in Fig.10) the line branches out to two hot wire thermal conductivity cells 2, charcoal trap 3, 2000 ml hydrogen storage bulb 4 and mercury manometer 5, these parts being required to determine the extent of the ortho-para conversion of the hydrogen to be used in the vapour pressure thermometer. The mercury

manometer of this thermometer is shown at 6. The pump also evacuates the bulb of the vapour pressure thermometer (through 3 mm. diameter german silver tube c) and two brass cans inside the cryostat (2, 3, and 4 respectively in Fig. 12). These cans can be filled with helium exchange gas stored in bulb 7, <sup>(Fig. 10)</sup> which is also of 2000 ml capacity. The Toeppler pump 8 transfers 200K equilibrium hydrogen from the catalyst (13 in Fig. 12) into the vapour pressure thermometer bulb. The measurement of the para content of the hydrogen is based on a method published by Grilly (1953a). A detailed discussion of the hydrogen modifications and their effect on the present work is given in Appendix 1.

The branch line to cell 27, the 2000 ml bulb 28 and the trap 29 serve in connection with the generation of pure oxygen following a method described by Hoge (1950a). The cell, diameter 2.5 cm, length 20 cm, is filled with about 100 g. of potassium permanganate and is heated with a small electric furnace (complete thermal decomposition of this quantity produces about 7 l. of gas at NTP which condenses to about 8 ml of liquid). The temperature of the salt is checked with a thermocouple inserted into the re-entrant well. Bulb 28 is filled with glass wool which stops manganese oxide dust while trap 29 serves for the condensation of the freshly prepared oxygen which is subsequently re-condensed into the vapour pressure thermometer bulb. If required, oxygen can be stored in the 2000 ml bulb 30.

While nearly all tubing and other parts of the first pumping line are made of pyrex glass, the second line connected



to rotary pump 9 is made almost entirely from copper tubing and the taps are standard refrigeration valves for in some sections of this line the pressure may rise to several atmospheres. The hydrogen for condensation is supplied from cylinder 13. It is freed from oxygen in a standard De-Oxo unit 14 where the oxygen combines with hydrogen in the presence of a catalyst to form water vapour. Moisture, carbon dioxide, etc. in the gas are condensed in a liquid oxygen trap 15 and residual impurities are absorbed in a charcoal trap 16 cooled by liquid nitrogen (Any such impurities other than helium will freeze before the hydrogen liquifies. If this happens in one of the capillaries shown in Fig. 12, blockages can occur which may cause serious trouble). The purified gas is compressed into reservoir 17 until the pressure, as read on gauge 18, reaches a predetermined figure corresponding to the quantity required for condensation. (846 ml of hydrogen gas at atmospheric pressure and 292°K condense into 1 ml of liquid at 20 K).

From reservoir 17 the hydrogen can flow either through another cooled charcoal trap 19 and tube F for condensation in the outer can of the cryostat (5 in Fig. 12) or it can branch off through a third charcoal trap 20 and capillary E to condense on the catalyst, being finally transferred into the vapour pressure thermometer bulb by means of the Toeppler pump (see above). The hydrogen can escape from the outer can of the cryostat (5 in Fig. 12) through tube G, a safety valve 10 being provided to prevent a

pressure build up above about 80 cm of mercury. Normally, the hydrogen is removed from the system through the pump return line 12 which extends to the roof of the building.

The helium is in a closed system (see Fig.11) connected to gas holders in another part of the building. This practice minimises the contamination of helium with other gases and its loss into the atmosphere (Broom and Rose-Innes 1956).

The system is evacuated by the rotary pump 1 (Fig.11). Helium gas can enter from the reservoir through tap 2 and copper tube L and gas or vapour can be pumped back along the same path. Liquid helium is transferred from a portable storage flask into the pyrex Dewar vessel 3 through opening 4 in the cryostat cover 5. (The section inside the Dewar vessel 3 is merely a symbolic representation of those parts directly relevant to the description of the helium circuit. All parts of the cryostat proper are shown in Fig. 12). Opening 4 is normally closed with a stopper and the Dewar vessel itself is sealed to the cover by a rubber sleeve 6 fastened tightly with iron wire clamps. When in use, the vessel 3 is surrounded by a second Dewar vessel 7 filled with liquid nitrogen to reduce heat influx by radiation. Because of the slight permeability of pyrex glass to helium vessel 3 must be re-evacuated after every experiment (see e.g. Giauque 1947).

The valve 8 or needle valve 9 or both together are used to regulate the suction of helium from the bath in the bottom of the Dewar vessel through capillary 10 and the two helium-

hydrogen heat exchangers 11 and 12. The mercury manometer 13 or the gauge 14 give a measure of the rate of flow of the helium vapour and consequently a measure of the rate of cooling of the hydrogen in the heat exchangers. The hydrogen gas enters these heat exchangers through tube F and the liquid collects in the container 15 which represents can 5 in Fig. 12. This method of attaining and maintaining the required low temperatures was based on a design published by Swanson and Stahl (1954). It also affords some measure of temperature control but must be supplemented by other control devices which will be described below.

b. The Cryostat. This is shown diagrammatically in Fig. 12. A copper block 1, diameter 3.5 cm., length 7.5 cm, contains the vapour pressure thermometer bulb 2 surrounded by four regularly spaced drills of 5.55 mm diameter providing a neat fit for the platinum resistance thermometers 16. The bulb as well as the thermometers are covered with silicone grease before insertion to improve the heat contact. (The slightly different original design of the block described in the second progress report was modified after the calibration of CT15 and CT16 mainly to make it easier to replace thermometers).

Surrounding the copper block are the three brass cans, 4 - 5. Can 3 is open to tube A and can 4 to tube B. Can 5, which holds the liquified hydrogen is open to tubes F and G. The

hydrogen gas enters the cryostat through tube F, circulates around liquid nitrogen tank 7 in  $2\frac{1}{2}$  mm copper tubing, then through the heat exchanger 8 made from 2 mm copper tubing, and enters the constricted upper portion of can 5 at 9. A heater wire of enamelled constantan SWG 42, 200 ohm is wound on to the vapour pressure line C to protect it from "cold spots".

The helium cooling line begins with the 0.5 mm thin walled copper-nickel alloy capillary 10 through which liquid helium is drawn up from the bath 11 into the heat exchange coil 12 ( $2\frac{1}{2}$  mm copper tubing) where it is vapourised. The vapour passes into heat exchanger 8 and is sucked out through tube K.

The neodymium oxide catalyst tube 13 inside can 5 is made from pyrex glass about 12 cm long and 1.2 cm diameter and is bent around the central copper tube just above the shoulder of can 4. It contains about two gram of oxide in the form of a fine powder which occupy approximately two-thirds of its volume. The 1 mm capillaries D and E are specially made from thin walled glass so as to present the smallest possible obstacle to the flow of hydrogen through tube G. To indicate the level reached by the condensed hydrogen, can 5 contains a gauge made of three 56 ohm Allen Bradley carbon resistors. The manner of using resistors as level indicators has been described by several authors (see e.g. Quinell and Futch, 1950).

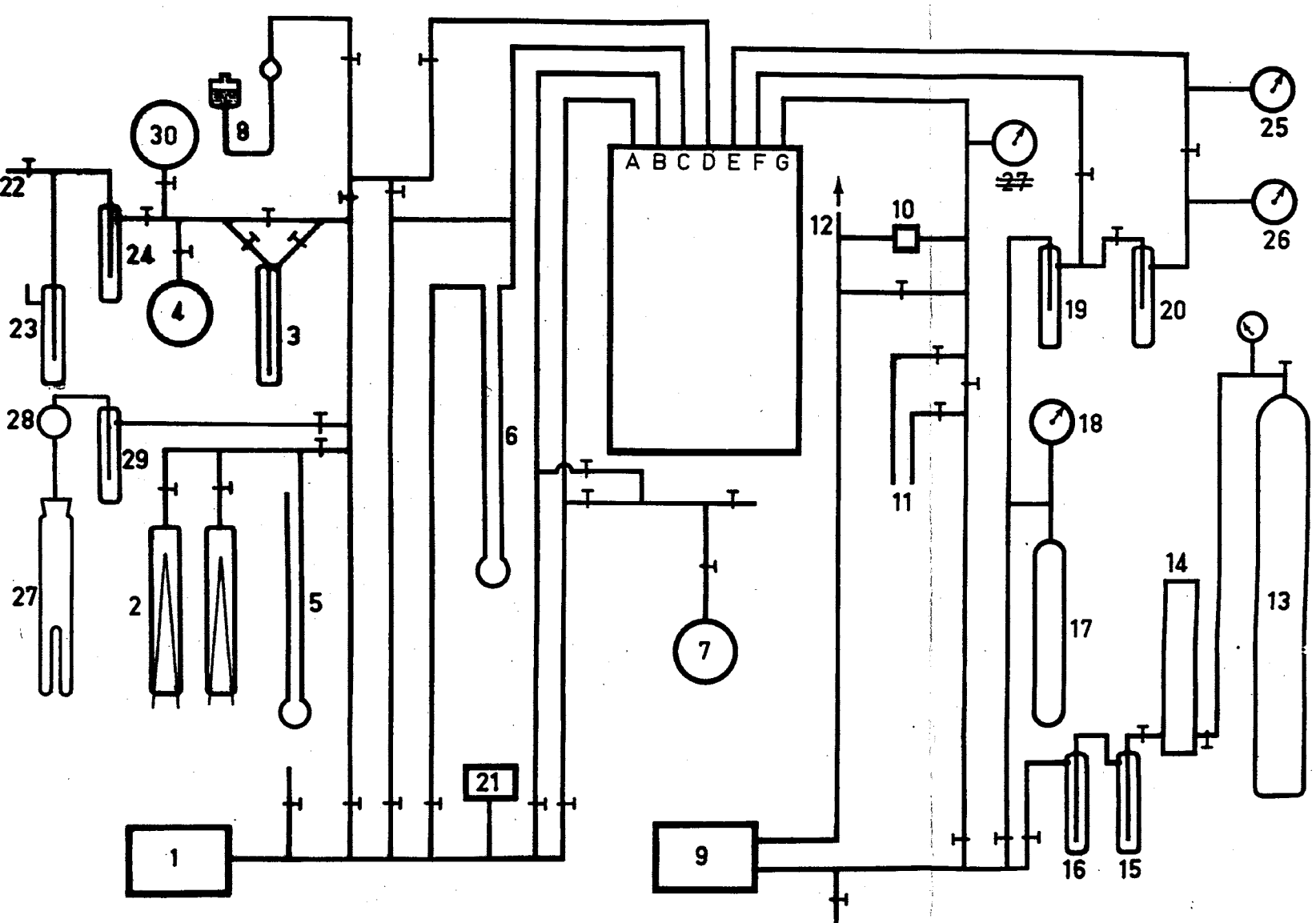


Figure 10. Pumping lines associated with Cryostat.

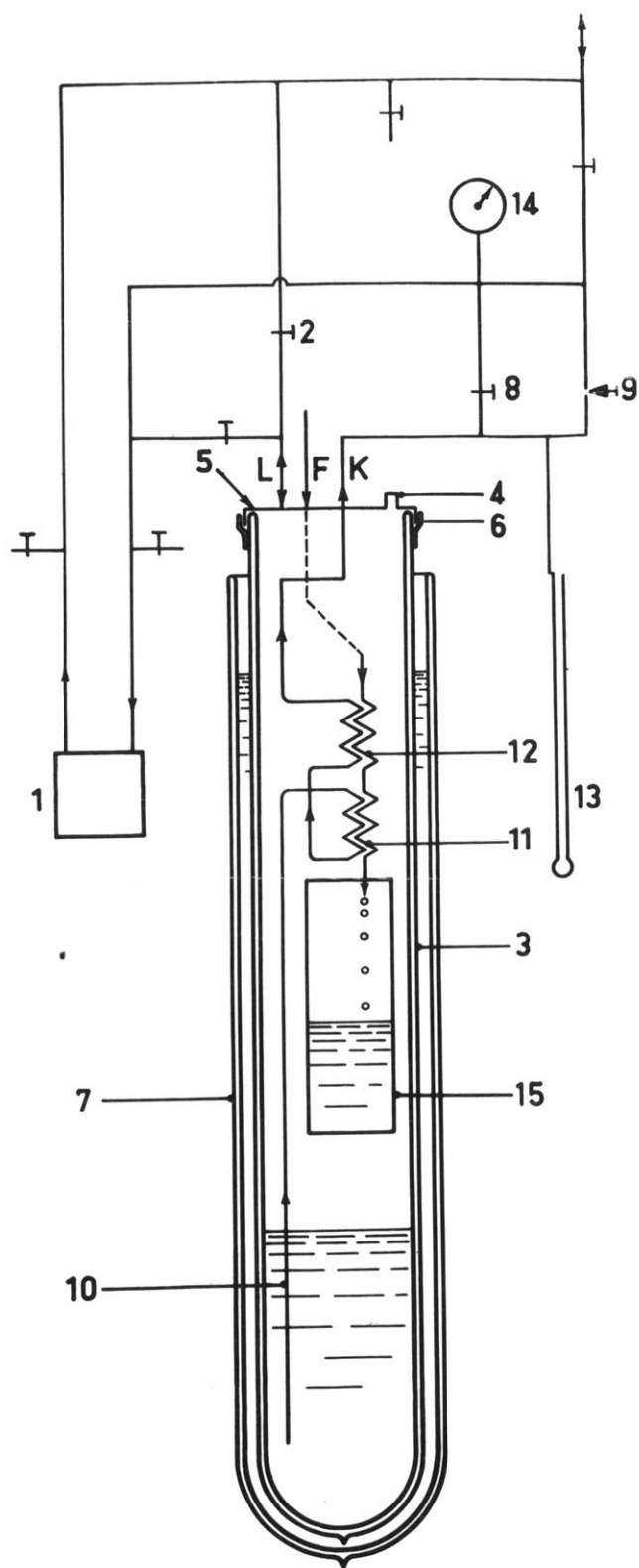


Figure 11. Schematic diagram of cryostat operation.

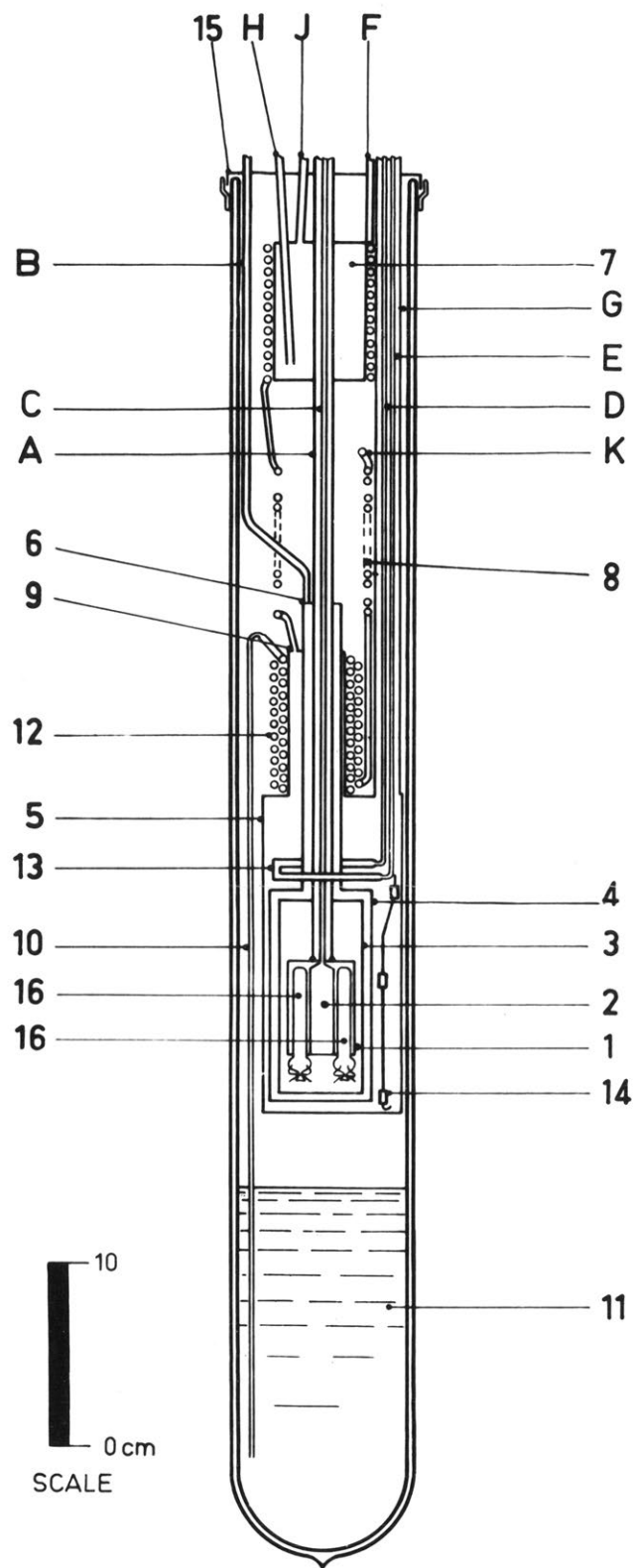


Figure 12. The Cryostat.



c. Temperature Control. Several devices are provided to maintain temperatures sufficiently steady to ensure thermal equilibrium during calibration. (1) Regulation of the rate of sucking up liquid helium into the heat exchangers as described in sub-section a above. (2) Regulation of the vapour pressure of the liquid hydrogen in can 5 using a manostat connected at 11 (Fig.10). This device blocks pump 9 whenever the vapour pressure drops below a reference level which can be selected anywhere within the range 5 to 740 mm Hg approximately. (3) Electronic temperature control actuated by the out of balance current from a Wheatstone bridge network.

To effect (3), two resistors, each about 600 ohm of SWG 42 enamelled constantan wire, are wound bifilarly and together over the surface of can 3, one of them to serve as a heater, and the other as the temperature sensitive element of the Wheatstone bridge circuit. A similar heater is also wound on the lower half of can 4 but in this case the sensitive element is made up of three carbon resistors each of 250 ohm and connected in series; one of them being placed in contact with the bottom of can 4, the others on either side about an inch up, reasonable temperature uniformity of the constantan and carbon resistors being ensured in this case by convection currents in the liquid hydrogen in which they are all immersed during operation. Heaters and sensitive elements are then connected to electronic control circuits designed to act in such a way that they compensate by a suitable heater current input the cooling effect of the helium

vapour to just the extent required to keep the temperature of copper block 1 sufficiently constant.

To provide an efficient path for the heat generated by the resistors, cans 4 and 3 as well as can 3 and the copper block 1, are connected by 1 cm wide copper braiding (not shown) soldered with Wood's metal into small holes drilled into the cans so that these solder joints can be made after the cans themselves have been soldered into position which is also done with Woods metal around their upper rims.

Method (1) soon proved inadequate by itself but gave quite good results when supplemented by a 500 ohm constantan wire heater wound around can 5; but even this set-up became unsatisfactory after CTL5 and CTL6 had been replaced with RL0 and DL.

To permit removal of the copper block, tube A is interrupted about 5 cm above this block by a copper joint and socket. Originally, the contact between the ground surfaces was poor, the weight of the block being supported almost entirely by capillary C. Hence with cans 3 and 4, evacuated the block was relatively isolated. After re-assembly the ground surfaces were pressed together, very firmly. This improved the heat contact so that with cans 3 and 4 evacuated sufficient heat reached the block to cause its temperature to rise relatively quickly to over 20°K. To stop this helium<sup>gas</sup> had to be admitted into can 4 at a critically small pressure otherwise the balance was upset in the opposite direction and heat was lost to heat exchanger 12

(Fig.12) so quickly that the temperature soon fell below  $14^{\circ}\text{K}$ . It was to remedy this that the devices described under (c) above were introduced. They have the added advantage of making temperature control more flexible. The constantan wire heater wound over the outside of can 5 is now used mainly to help raise the temperature of the apparatus when required.

It must still be mentioned that, in order to minimise all uncontrolled heat transfer into the cryostat all metal tubes to the cans are made of a poorly conducting copper-nickel alloy from the cover 15 down to the lower end of heat exchanger 8. Below that copper tubes are used to facilitate realisation of as uniform as possible a temperature distribution in that region.

d. Modifications for work in the liquid oxygen range (about  $54^{\circ}$  to  $90^{\circ}\text{K}$ ). Pure oxygen for the vapour pressure thermometer is prepared as described in sub-section a above. Temperatures above the boiling point of nitrogen (about  $77.5^{\circ}\text{K}$ ) are realised by filling Dewar 3 (Fig.11) with the appropriate mixture of commercial liquid nitrogen and oxygen, pure oxygen being condensed into the vapour pressure thermometer bulb as soon as the temperature of the copper block is sufficiently low.

For measurements below  $78^{\circ}$  commercial oxygen is now condensed into can 5. The pressure over this oxygen is reduced

simultaneously with that over the liquid in Dewar 3 until the required temperature is reached which is then maintained with the help of manostat 11 (Fig.10).

## VI. PROCEDURE, RESULTS AND COMMENTS.

(i) Low Temperature.-- In this region the procedure is as follows; Hydrogen gas to a pressure of a few millimeters of mercury is admitted into dewar 3 (Fig.11) and a little helium gas into cans 3, 4, 5 (Fig.12). The temperature of the cryostat assembly is then lowered to near 90°K by keeping dewar 7 (Fig.11) and tank 7 (Fig.12) filled with liquid air, this degree of pre-cooling being desirable to avoid wasting liquid helium. Dewar 3 is now thoroughly evacuated and then filled with liquid helium first level with the bottom of can 5 and a little later to the level of heat exchanger 8 (Fig.12) In these conditions the copper block soon reaches the temperature of the boiling helium and this temperature is measured using manometer 13 (Fig.11) as a vapour pressure thermometer and a table published by Linder (1950) to obtain the temperature from the indicated pressure. The resistance of the thermometer is read simultaneously. \*

Now helium is allowed to boil off until its level is back to below can 5 which is then filled with liquid hydrogen, the condensing process occurring in heat exchanger 12. Next hydrogen is condensed into the catalyst tube 13 (Fig.12) and when fully

---

\* Near 4°K  $dw/dT$  is so small that effects due to differing impurity contents can be safely ignored at least for the purposes of work above 14°K. Consequently,  $z$ , which is obtainable only by extrapolation can be replaced by  $w_{4.2}$  which is readily and accurately measurable. Throughout this work,  $w_{4.2}$  is being used, therefore, rather than  $z$ .

catalysed, transferred from this tube into the vapour pressure thermometer bulb 2 (see also Appendix 1). A temperature in the range  $14^{\circ}$  to  $20.4^{\circ}$  is now selected and once this has become sufficiently steady, simultaneous readings are taken of the vapour pressure of the hydrogen (using a cathetometer with a range of 800 mm. and a least count of 0.01 mm) and the resistance of the thermometer. However, this direct calibration was carried out only on thermometers CT15 and CT16. Results for the other thermometers were obtained by direct or (in the case of D1) indirect intercomparison with CT15.

Temperatures were calculated from the vapour pressure readings using the vapour pressure - temperature scale published by Wooley et al. (1948). A scale published later by Hoge and Arnold (1951) agreed with the Wooley scale below  $17^{\circ}\text{K}$  but was  $0.002^{\circ}$  lower at  $18^{\circ}$  and  $0.005^{\circ}$  lower at  $20^{\circ}\text{K}$ . Since in this region both scales were based on the Hoge and Brickwedde (1939) temperature scale, Hoge and Arnold could give no reason for these differences.

Both apparatus and procedure are rather complicated and the first two attempts to work the cryostat had to be abandoned before readings could be started. After several adjustments a third attempt was more successful giving a fairly reliable reading near the triple point where the temperature could be kept reasonably steady but less reliable ones at the higher temperatures where conditions were less favourable (H3, Table 4).

Table 4

Results of the Calibration of CT15 in the  
Liquid Hydrogen Region.

Reference	No.	measured		interpolated		$W_{\text{Ch6}} \times 10^4$	$W_{\text{CT15}} - W_{\text{Ch6}}$ $\times 10^4$
		T °K	$W \times 10^4$	T °K	$W \times 10^4$		
H 3 25.3.57	1	13.83	15.20	14.00	15.64		
	2	16.50	23.88	17.00	26.08		
	3	17.83	30.24	18.00	31.16		
	4	18.25	32.52	18.00	31.15		
H 4 30.5.57	1	13.975	15.56	14.000	15.62	14.42	1.20
	2	14.759	17.75	14.800	17.87	16.66	1.21
	3	16.998	26.20	17.000	26.22	25.02	1.20
	4	19.385	39.58	19.400	39.68	38.49	1.19
	5	20.052	44.28	20.000	43.90	42.72	1.18
	6	20.126	44.86	20.100	44.65	43.45	1.20
H 5 27.6.57	1	16.277	23.11	16.200	22.80	21.58	1.22
	2	16.370	23.50	16.400	23.62	22.40	1.22
	3	18.056	31.53	18.000	31.23	30.04	1.19
	4	18.923	36.62	19.000	37.11	39.91	1.20
	5	19.944	43.56	20.000	43.96	42.72	1.24



A heater wire was then wound on to can 5, the heat input being controlled manually to balance the cooling effect of the helium vapour. This led to a considerable improvement in temperature control so that the two following calibrations gave satisfactory and consistent results excepting only the  $20^{\circ}$  readings which differed by about  $0.003^{\circ}$  but there the  $20.1^{\circ}$  result indicates that the correct value is likely to lie close to the mean of the two divergent readings (see H4, H5, Table 4). There can be little doubt that the differences between these calibrations and H3 are due entirely to the absence of adequate temperature stability in the latter case.

Inspection of the calibration results for CT15 soon showed that  $(dw/dT)_{CT15}$  was virtually equal to  $dw/dT$  of the Russian thermometer Ch6 (see Table 2) and this for the entire range  $14^{\circ}$  to  $20^{\circ}\text{K}$ . Hence  $(dw/dT)_{Ch6}$  could be used safely with the CT15 values at least for the short interval between the calibration temperature and the nearest  $0.1^{\circ}$ . The results of these calculations are shown in Table 4 : the averages at each calibration point are given in the column "measured", the others in the column "interpolated"; for comparison the corresponding Ch6 values are entered in the next column. The difference shown in the last column are sufficiently equal to justify the use of the same procedure also for the somewhat larger temperature intervals such as that from  $14.8^{\circ}$  to  $15^{\circ}$ . The results for this thermometer are shown in the CT15 column of Table 6.

Table 5 Comparison between CT 15 and CT 16  
in the Liquid Hydrogen Region.

Reference	No.	T °K	$W_{CT16} \times 10^4$	$W_{CT15} \times 10^4$	$W_{CT16} - W_{CT15}$ $\times 10^4$
H 4 30.5.57	1	14.000	15.73	15.62	0.11
	2	14.800	18.00	17.87	0.13
	3	17.000	26.34	26.22	0.12
	4	19.400	39.79	39.68	0.11
	5	20.000	44.03	43.90	0.13
H 5 27.6.57	1	16.200	22.92	22.80	0.12
	3	18.000	31.36	21.23	0.13
	4	19.000	37.22	37.11	0.11
	5	20.000	44.03	43.96	0.07

Average Difference :

0.12

Concerning CT16 the similarity of its results with those of CT15 was fully expected in view of their nearly identical ITS constants and this is demonstrated in Table 5. The CT16 column in Table 6 was then obtained by adding  $0.12 \times 10^{-4}$  to each  $w_{CT15}$  value.

After further calibration in the liquid oxygen region (see below) thermometers CT15 and CT16 were replaced by D1 and R10. However, the calibration of these instruments was not successful, the data obtained being useful only for intercomparison purposes (Fig.13). The failure of these experiments led to the further changes in the apparatus described above (V, iii, b and c).

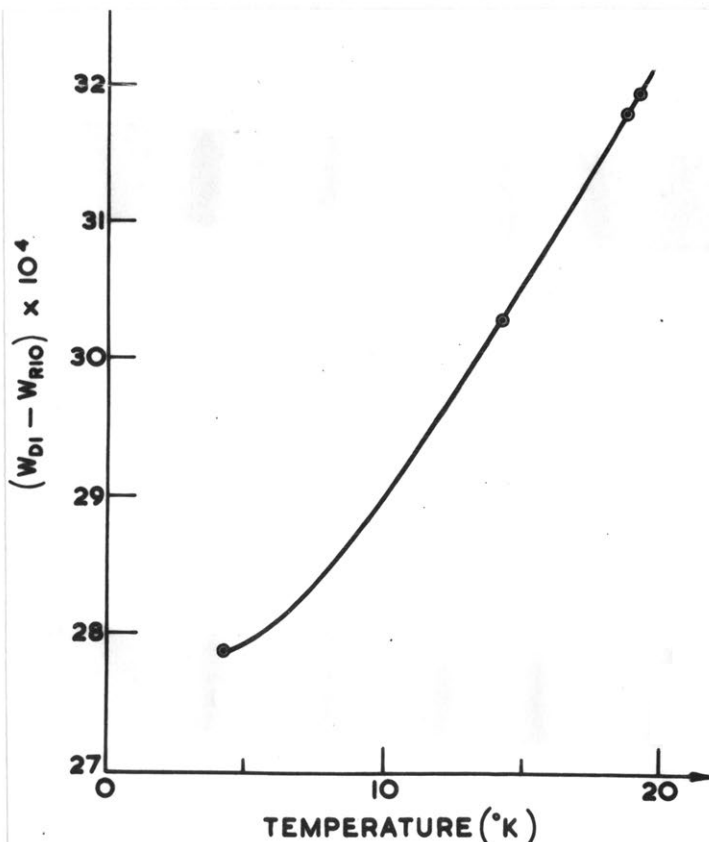


Figure 13. Comparison between thermometers R10 and D1 between 4.2° and 20°K.

Table 6

Liquid Hydrogen Region. Calibration Results.

Summary.

No.	CT 15	CT 16	CT 18	R 10	D 1
$R_{0^{\circ}\text{C}}(^{\circ}\Omega)$	22.8289	22.605 <sub>4</sub>	23.2602	23.5680	25.774 <sub>5</sub>
$R_{100^{\circ}\text{C}}/R_{0^{\circ}\text{C}}$	1.39257 <sub>7</sub>	1.39256 <sub>2</sub>	1.39237 <sub>4</sub>	1.39113 <sub>0</sub>	1.38976

T $^{\circ}\text{K}$	W $\times 10^4$				
4.24	6.39 <sub>0</sub>	6.50 <sub>0</sub>	8.90 <sub>0</sub>	16.09 <sub>3</sub>	43.97 <sub>1</sub>
14	15.62	15.74	18.85	27.17	57.47
15	18.50	18.62	21.83	30.41	61.01
16	22.02	22.14	25.45	34.31	65.25
17	26.22	26.34	29.77	38.90	70.19
18	31.23	31.35	34.89	44.34	75.95
19	37.11	37.23	40.89	50.69	82.65
20	43.92	44.04	47.82	58.00	90.30

The final series of experiments were made with CT15 R10 and the newly completed thermometer CT18. It was started with a check calibration of CT15. Unfortunately, just prior to the experiment the heater around the vapour pressure thermometer tube C open circuited and when the results were worked out, it was found that the temperatures corresponding to each of the measured resistance values were between  $0.05^{\circ}$  and  $0.03^{\circ}$  lower than during calibrations H4 and H5 which suggested the presence of "cold spots" during the last calibrations. Subsequent tests near  $60^{\circ}\text{K}$  confirmed that "cold spots" leading to errors between  $0.05^{\circ}$  and  $0.1^{\circ}$  could have occurred in the conditions in which the equipment was operated. Since, as is evident from Table 4, the standard of the earlier results was such that a check was by no means imperative (the principal objective of the final series was an intercomparison between CT15, CT18 and R10) it was decided not to repeat the attempt but to accept the results of calibrations H3 and H4 (Table 4) as final.

Results of the intercomparisons as collected in Table 6 were obtained by plotting the differences CT18 - CT15, and R10 - CT15, and D1 - R10, as a function of temperature and drawing a smooth curve through the resulting points (Figs.13,14). Some of the points in Fig. 14 near and above  $20^{\circ}\text{K}$  were taken within a relatively short time interval; some soon after a

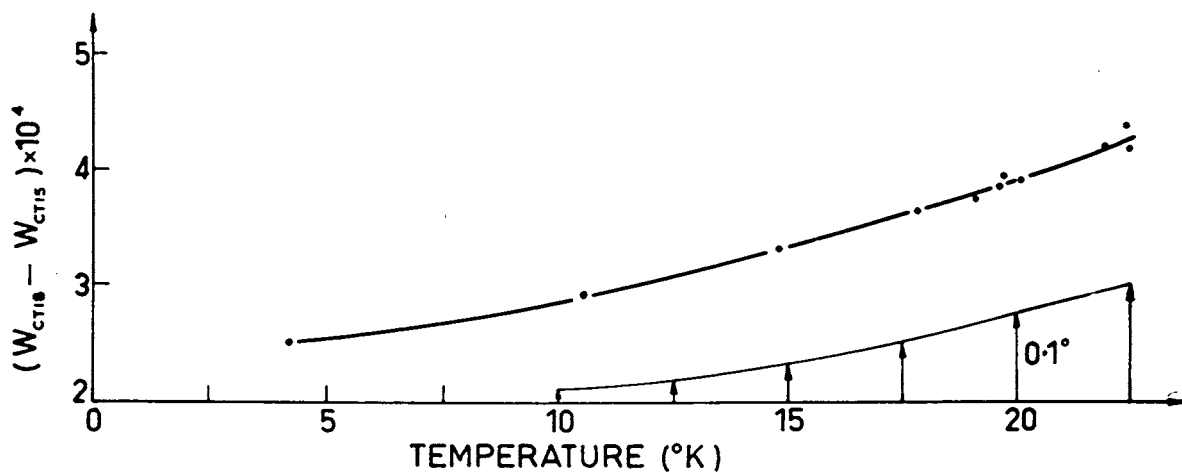
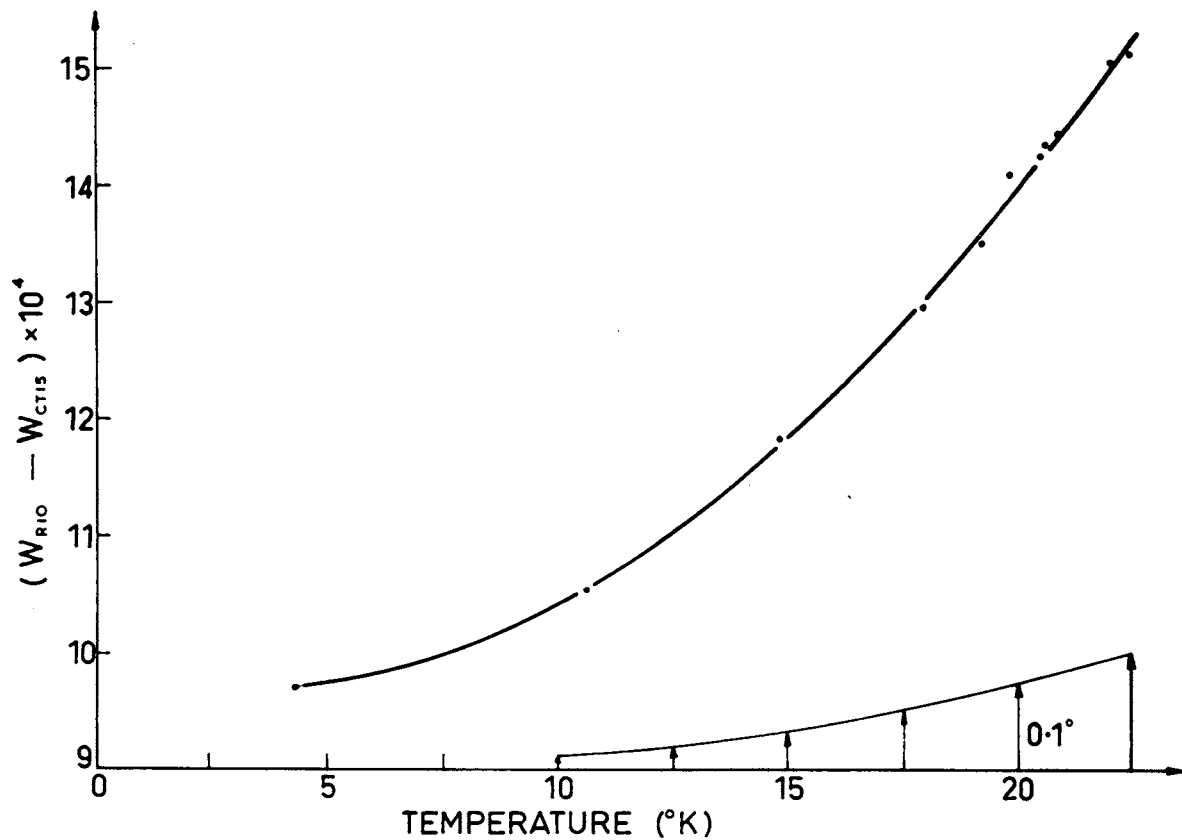


Figure 14. Results of intercomparisons of CT15 with CT18 and R10.

rise and others soon after a fall in temperature. Although conditions were ~~found~~ nearly steady during each reading, it is possible that this near steadiness did not always indicate true equilibrium which would then account for the relatively large scatter.

(ii) The Range  $54^{\circ}$  to  $90^{\circ}\text{K}$ .-- Procedure in this region has been largely described in conjunction with the description of the equipment (V, iii, d above). All temperatures were calculated from the vapour pressure - temperature relationship published by Hoge (1950a).

From  $90^{\circ}$  to  $78^{\circ}\text{K}$  every thermometer was calibrated directly against the oxygen vapour pressure thermometer. Below  $78^{\circ}\text{K}$  only CT15 and CT16 were calibrated directly. Results for CT18 and R10 were again obtained by intercomparisons with CT15. Work in this latter region becomes progressively less accurate because, as shown in Table 7, below about  $75^{\circ}\text{K}$  the vapour pressure of oxygen changes only very little with temperature.

Table 7. Approximate Values of  $dP/dT$  for the Vapour Pressure of Liquid Oxygen as a Function of  $T$ .

$T$ ( $^{\circ}\text{K}$ )	$dP/dT$ (mm Hg/ $^{\circ}\text{K}$ )
90	75
85	50
80	30
75	17
70	8
65	4.5
60	1.3
55	0.4

A typical set of calibration results for CT15 is given in Table 8. Altogether, between 50 and 60 such readings were taken, not all, however, proved acceptable since the temperature was not always adequately stable.

Table 8. Results of the Calibration of CT15 in the Liquid Oxygen Region.

T (°K)	w
89.932	0.242840
87.201	.230922
86.211	.226612
85.837	.224970
83.429	.214514
81.923	.207960
80.293	.200886
78.576	.193425
76.227	.183275
73.100	.19984
71.410	.16260
68.585	.15051
63.49	.12894
60.07	.11486
54.38	.09290

To obtain degree by degree results,  $dw/dT$  values for the most stable readings were plotted against T (Fig.15) and a smooth curve was drawn through these points which was then used for interpolation. The results of this interpolation are shown in Table 9. It was again found that at least below 80°K  $(dw/dT)_{CT15}$  was very similar to  $(dw/dT)_{CH_6}$  and this fact was used to obtain whole number values at and below 65°K.



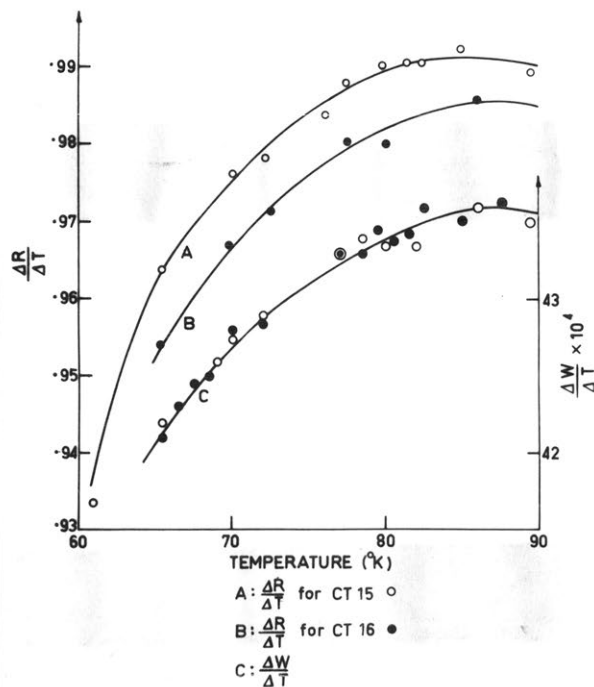


Figure 15.  $dR/dT$  and  $dw/dT$  for CT15 and CT16 between 65° and 90°K.

Table 10 shows a comparison between the relative resistances of CT15 and CT16 where both were measured at the same or nearly the same temperature. It is evident that the virtually constant value of this difference already noted in the liquid hydrogen region is maintained right up to 90°K, the maximum variation from the average difference being again equivalent to little more than 0.002°. Consequently, the figures for CT16 in Table 11 below were again obtained by adding the average difference to the corresponding value for CT15.

Table 10.  $w_{CT16} - w_{CT15}$  (  $w$  ) in the range 62° to 90°K

$T^{\circ}K$	$w \times 10^4$	$T^{\circ}K$	$w \times 10^4$
62	0.1	78	0.25
68	0.0	81	0.20
71	0.1	83	0.10
73	0.2	86	0.15
76	0.1	90	0.20

Smoothed results for all thermometers at 5° intervals are given in Table 11. Intermediate values above 65°K can be obtained using Table 9 in conjunction with the curves shown in Figure 16. No comparisons could be made between 23° and 53° but in view of the fairly well defined directions of the curves near 20° and 55° respectively, it seems unlikely that measured values in this range would have shown significant differences from the tentative values shown in the graph. This should be true especially for R10.\*

Figure 16 affords an excellent illustration of the difficulties inherent in the task of finding as it were a common denominator valid for at least a fair proportion of  $w - T$  relationships of platinum thermometers. For comparisons, the  $w - T$  relationships for T4 (White and Woods) and L6 (Hoge

---

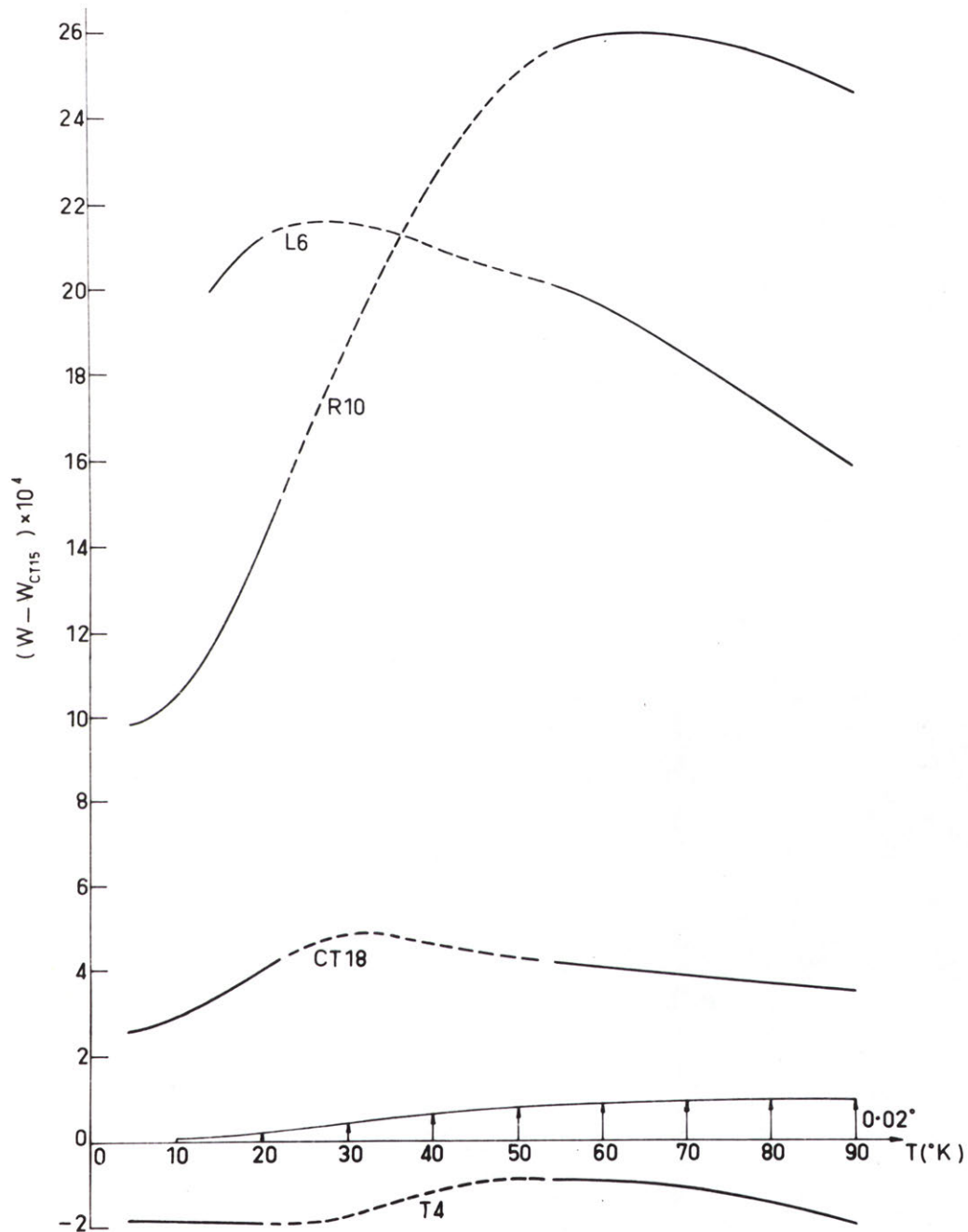
\* In the light of subsequent developments (see VII, ii, below) measurements in the neon range (24.5° to 27°K) might have proved very useful but this could not have been anticipated, of course. In any case, this range is not nearly as well known as that of hydrogen and oxygen (Hoge 1941) and it is more than doubtful whether such measurements would have repaid the considerable extra demand on materials and time which they would have required. It was for this reason that no provisions were made for them in the first instance.

Table II

Calibration in the Liquid Oxygen Range.

Summary for 5° Intervals.

T (°K)	$w \times 10^4$				
	CT15	CT16	CT18	R10	D1
55	1005.6	1005.8	1009.6	1031.3	-
60	1145.8	1146.0	1149.8	1171.9	-
65	1353.4	1353.6	1357.3	1379.6	-
70	1565.4	1565.6	1569.2	1591.5	-
75	1780.0	1780.2	1783.7	1805.8	-
80	1996.20	1996.35	1999.80	2021.65	2044.55
85	2213.45	2213.60	2216.95	2238.55	2271.00
90	2431.40	2431.55	2434.80	2456.00	2477.60



THE DOTTED SECTION OF EACH CURVE  
WAS OBTAINED BY GRAPHICAL INTER-  
POLATION.

Figure 16. Differences in relative resistances with  
CT15 as standard.

and Brickwedde) relative to CT15 have been added to those for CT18 and R10 and it is seen that at least below about 55°K everyone of these curves has its own characteristic shape. The  $w - T$  curve of R10, although not typical, nevertheless serves a useful purpose since it indicates that it is not always possible to rely on the characteristics of an instrument above 90°K when trying to predict its behaviour below 90°K.

(iii) Reliability of Results.- Resistance measurements were made in general to  $\pm 0.00005$  ohm (equivalent to about  $\pm 0.02 \times 10^{-4}w$ ) and their reproducibility in the hydrogen range was of about the same order as is indicated by the degree of consistency of the results in Table 4. In the oxygen range reproducibility was found to be close to  $\pm 0.0001$  ohm corresponding to  $\pm 0.001^\circ$ . Except at the ITS calibration points the resistance was always less than about 6 ohm so that no measurement was made to much better than 1 part in  $10^5$ . The absolute accuracy to which the resistors are known is probably better than this figure.

Pressure readings are believed to be reliable to at least  $\pm 0.02$  mm, the uncertainties in the meniscus correction and other corrections being generally much less than this figure. For the measurement near the triple point of oxygen the pressure reading was probably accurate to  $\pm 0.01$  mm.

Coming to the quality of the gases used for condensation in the vapour pressure thermometer, the effect of residual impurities in the hydrogen should be negligible on account of

their low vapour pressures below  $20^{\circ}\text{K}$ . Contamination of hydrogen by helium (or vice versa) is prevented by keeping the helium in an entirely separate circuit (see Fig.11). Regarding the completeness of the  $\text{nH}_2 - \text{eH}_2$  transition this was checked by drawing samples from the catalyst tube over a period of about eight hours. No significant changes in the thermal conductivity of these samples were observed after the first 45 minutes approximately. (See Appendix 1, Fig.A4). Transfer from catalyst tube 13 into the vapour pressure thermometer bulb 2 (Fig.11) took place generally about 2 hours after charging the catalyst and after pumping off approximately half the amount of liquid originally condensed.

As to the purity of the oxygen, measurements with four different samples prepared each time from fresh amounts of reagent, gave results agreeing to  $\pm 0.001^{\circ}\text{C}$ . Storing the gas for several weeks in bulb 30 (Fig.10) had no significant effect on vapour pressure readings.

Temperatures, therefore, must be considered reproducible to within a few millidegree near and below  $20^{\circ}\text{K}$  and to about a millidegree between  $75^{\circ}$  and  $90^{\circ}\text{K}$ . Below  $75^{\circ}$  reproducibility falls and near  $55^{\circ}$  it is only about  $\pm 0.025^{\circ}$  (see Table 7).

While comparisons with thermometers calibrated on the same vapour pressure scales should give agreement substantially equal to the reproducibility figures just quoted, the position could be different concerning agreement with thermometers calibrated on other scales which could differ from the Wooley and Hoge scales and, therefore, from the N.B.S. Provisional

Temperature Scale by  $0.02^{\circ}$  or even more seeing that the agreement claimed to exist between any one of the published gas thermometry scales and the Thermodynamic Scale is never better than  $\pm 0.02^{\circ}$ .

(iv) Remarks on  $dw/dT$  near  $90^{\circ}\text{K}$ .-- Los and Morrison (1951) observed that for their thermometers  $dw/dT$  as obtained from gas thermometric measurements near  $90^{\circ}\text{K}$  did not agree with  $dw/dT$  as calculated from the Van Dusen equation (3). This is true also for the present work. The explanation for the discontinuity in  $dw/dT$  at  $90.19^{\circ}$  is found in the fact that  $d^2w/dT^2$  changes sign only a few degrees lower down (see Table 1). Not surprisingly, this change affects  $w - T$  curves even above  $90^{\circ}\text{K}$  and this effect cannot be expected to be reproduced exactly by a formula based largely on the more uniform  $w - T$  characteristics of platinum at much higher temperatures. It would then appear that the ITS could not be extended downwards without introducing a discontinuity at least in  $dw/dT$  unless equation (3) could be suitably modified to obtain better agreement than exists at present between this section of the ITS and the Thermodynamic Scale (see also Keesom 1939).

In addition to this discrepancy, there is another one between the  $dw/dT$  values resulting from the present investigation and those obtained during the various gas thermometric measurements listed in Table 2.





All gas thermometric measurements show that the maximum reached by  $dw/dT$  values just below  $90^{\circ}$  is the higher the purer the platinum. The highest recorded value is that for the Russian thermometer Ch6 reaching  $43.46 \times 10^{-4}$  between  $87^{\circ}$  and  $88^{\circ}$ , while  $(dw/dT)_{L_6}$  reaches only  $43.44 \times 10^{-4}$ . Against this CT15 which is certainly if anything less pure than CH6 nevertheless has a  $(dw/dT)_{\max.}$  of nearly  $43.7 \times 10^{-4}$ , an extremely high value. Even R10 which is made from relatively impure platinum has a  $(dw/dT)_{\max.}$  of  $43.5 \times 10^{-4}$ .

It seems most likely that this irregular behaviour must be due to an irregularity in the Hoge vapour pressure scale affecting the region between about  $83^{\circ}$  and  $90^{\circ}\text{K}$ . It is noteworthy that the Hoge scale and the Henning and Otto (1936 c) scale (although both use the same temperature for the boiling point of oxygen) disagree strongly and, what is more important for the present purpose, non-uniformly in this very region (see Fig.17) If  $w_{CT15}$  is calculated from the Henning and Otto scale instead of the Hoge Scale,  $dw/dT$  values are in much better agreement with the gas thermometric results including those by Hoge and Brickwedde (1939) themselves, although the Hoge vapour pressure scale was set up using Hoge and Brickwedde's temperature scale. Notwithstanding these irregularities, the Hoge Scale was

retained for this work for on the whole it is likely to be the more accurate of the two.

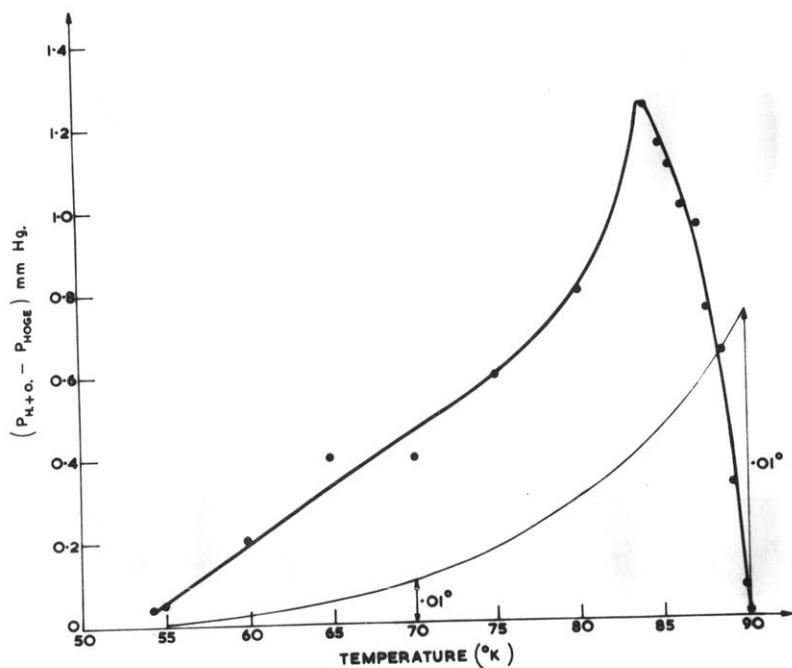


Figure 17. Differences between the  $O_2$  vapour pressure scales of Henning and Otto, and Hoge.

## VII. THE CORRELATION OF $w - T$ DATA.

(i) Some Characteristics of Platinum Thermometers.— This subject will now be investigated using the data accumulated in Sections III, IV, and VI, though unfortunately many of the published  $w - T$  tables do not even indicate the  $\alpha$  of the thermometer, let alone its  $w_{4.2}$  value.

(a) The  $\alpha - w_{4.2}$  relationship. A high  $\alpha$  value is the accepted ITS criterion for the purity of platinum (see e.g. ITS 1948, Part IIa) and the degree of validity of this criterion is illustrated in Fig. 18A where  $\alpha$  is plotted against  $w_{90.19}$  for 19 thermometers differing widely in origin and purity;  $w_{90.19}$ , of course, should be the smaller the purer the platinum (see III, ii above). This relationship is found to be generally true although there are some "local" exceptions such as the pair T4 and 58 or the pair F and 9. It is interesting to note that at least some of the thermometers with "anomalous"  $w_{20}/w_{90}$  values such as L9 and E also have  $\beta$  values outside ITS requirements. (Fig. 18A was also used to obtain  $\alpha$  for thermometers Ch6, L6 and 204).

A similar relationship to that between  $\alpha$  and  $w_{90}$  might be expected to hold also between  $\alpha$  and  $w_{4.2}$  but Fig. 18B shows that here there are many serious exceptions. The reason for most of these exceptions is soon seen to lie in the shape of the low temperature  $w - T$  curves of the affected thermometers. These curves show sections with exceptionally high  $dw/dT$  values, thermometers 59 (Fig. 6) and R10 (Fig. 16) being here the most striking examples. Referring to Section III(iv) it seems likely that the platinum of these

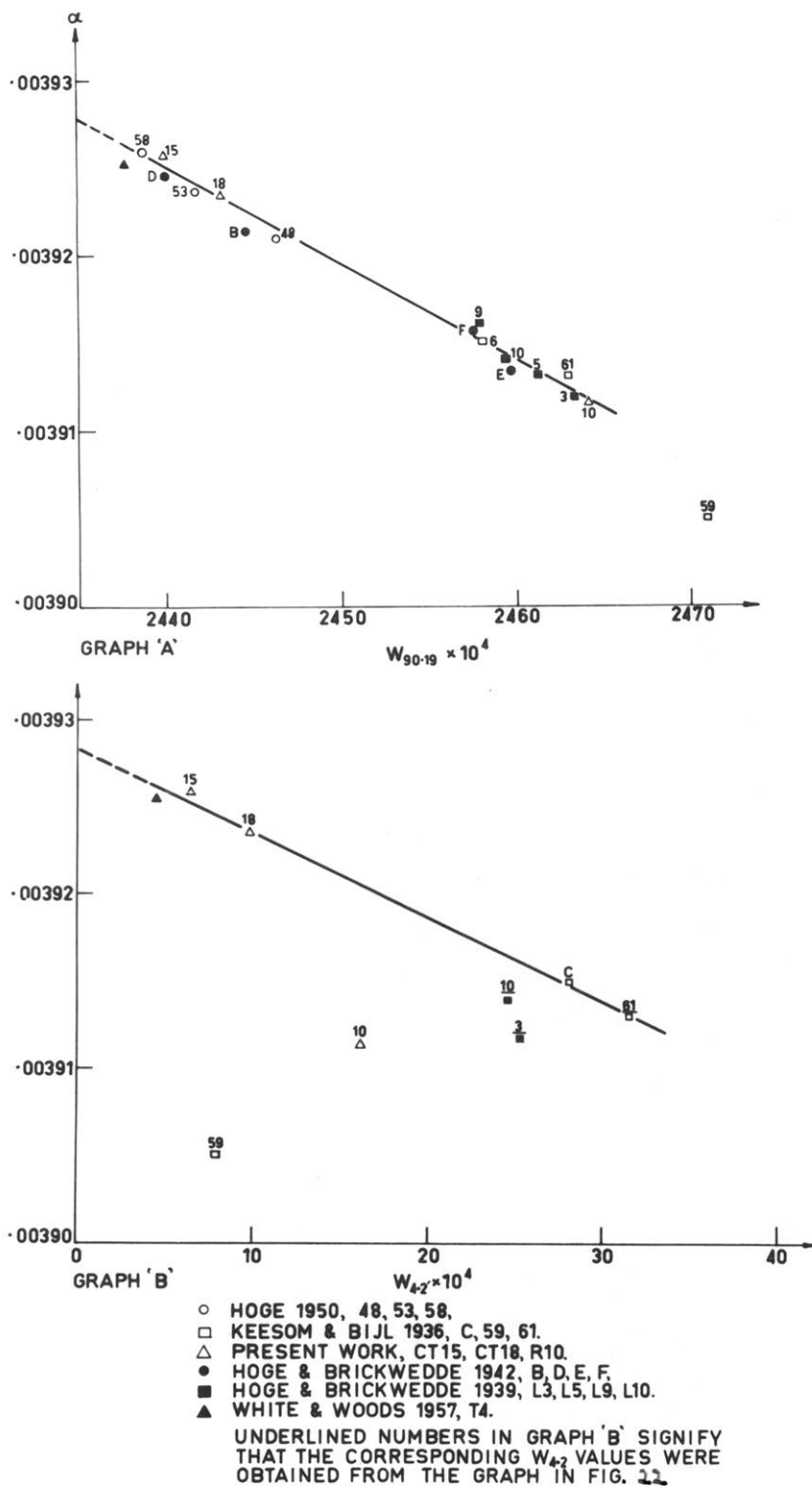


Figure 18. Graph A. The relationship between  $\alpha$  and  $w_{90.19}$

Graph B. The relationship between  $\alpha$  and  $w_{4.2}$

5457-5

instruments had been contaminated by elements with widely differing valencies. Such an assumption is supported by the fact that the platinum for 59 was made by the thermal decomposition of  $\text{Pt CO Cl}_3$ .

In addition there are some irregularities in the region of very high  $\alpha$ . Thus, available data indicates - but this could not be shown in Fig. 18B - that for Los and Morrison's thermometers the general rule that  $\alpha$  increases while  $w_{4.2}$  decreases, is replaced by  $\alpha$  and  $w_{4.2}$  increasing together.

It appears from Fig. 18B that sets of thermometers similarly affected by impurity contents (they would then obey the assumptions made by Hoge) would have certain characteristic  $\alpha/w_{4.2}$  values. These values, therefore, should prove a simple and effective criterion for the selection of thermometers likely to show similar behaviour in the low temperature region and consequently also likely to obey reasonably simple interpolation formulae to a sufficient degree of accuracy. In other words, the ratio could play a similar part for low temperature thermometry which is now played by  $\alpha$  above 90°K so that only those thermometers would be acceptable for low temperature work whose  $\alpha/w_{4.2}$  values fall within definite limits. It would then be possible that a thermometer could be rejected because its  $\alpha$  value is relatively too high. Hoge's results (see iii, a, below) and those obtained during the present work suggest that it should be possible to fix the criterion such that it would be both narrow enough to fulfil its purpose and yet be satisfied by a sufficiently large number of instruments.

The ratio could be expressed in the form

$$\frac{\alpha}{w_{4.2}} = \left( a + \frac{b}{w_{4.2}} \right) \pm e \quad (18)$$

The precise value of these constants could be fixed only after an analysis of  $\alpha$  and  $w_{4.2}$  values for a sufficiently large number of thermometers (Stimson 1952). Using the few results available at present leads to

$$\frac{\alpha}{w_{4.2}} = \left( -4.55 \times 10^{-3} + \frac{0.0039277}{w_{4.2}} \right) \pm 0.00018 \quad (18a)$$

but these values can be regarded as no more than tentative.

In general equipment suitable for measurements near  $20^{\circ}$  will be easily adapted for measurements near  $4.2^{\circ}$ . Failing this, the ratio  $\alpha/w_{4.2}$  could possibly be replaced or just supplemented by the ratio  $w_{20}/w_{90}$  for  $w_{20}$  rises in most cases fairly regularly with  $w_{4.2}$  (see Fig. 23 below) while the near proportionality between  $w_{90}$  and  $\alpha$  has just been demonstrated. The effectiveness of  $w_{20}/w_{90}$  for the present purpose can be judged from Fig. 19 where  $w_{20}$  is plotted against  $w_{90}$  for 15 thermometers. The straight line in this figure is so drawn that it passes through the positions of Ch6 and L6 (see also Fig. 21 below).

The ratio  $w_{20}/w_{90}$  should be as effective for the present purpose as  $\alpha/w_{4.2}$  although this latter ratio is basically more satisfactory. Against this,  $w_{20}/w_{90}$  can be determined without the need for an additional calibration point.

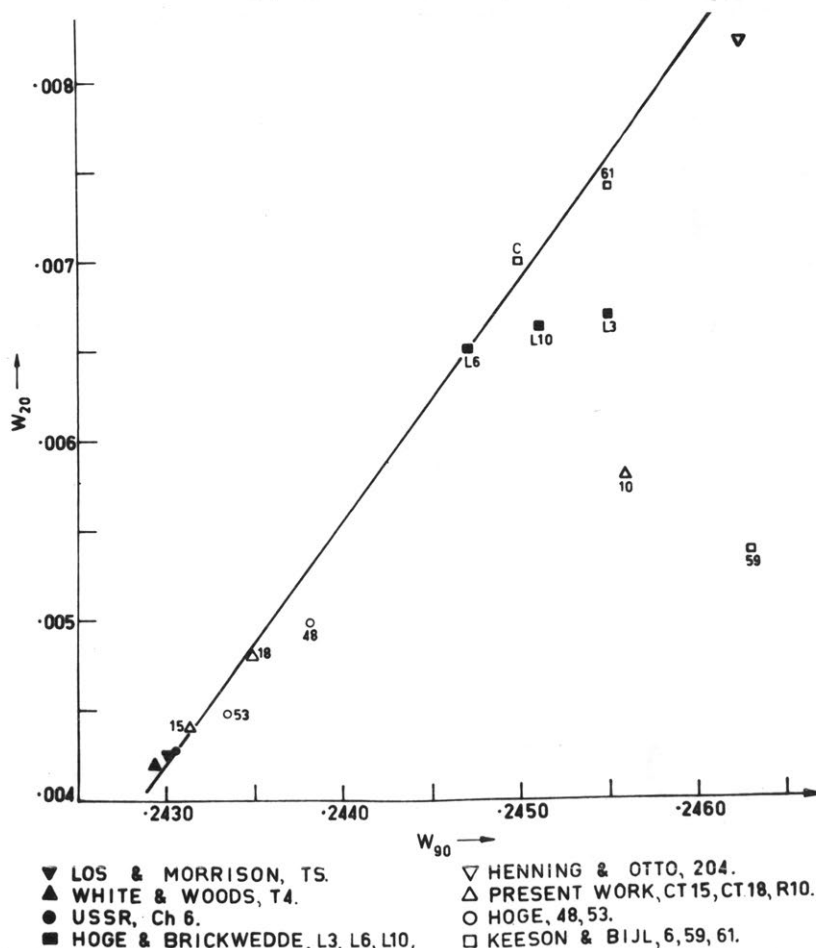


Figure 19.  $w_{20}$  as a function of  $w_{90}$ .

(b) Properties of  $dw/dT$ . Figure 20 shows smoothed differences between  $dw/dT$  for a few thermometers varying in impurity content and  $dw/dT$  for an ideally pure instrument as obtained by extrapolation, these differences being plotted against temperature (see Fig. 1 for the shape of the  $dw/dT$  versus  $T$  curve).

The following facts are apparent. Firstly,  $dw/dT$  is greater for the purer thermometers only above about 26°K. Below 26° it is the smaller the purer the metal. No doubt the occurrence of this inversion is one of the principal reasons for the difficulties encountered by all attempts at extending ITS methods below 26°. Secondly, it is below this inversion



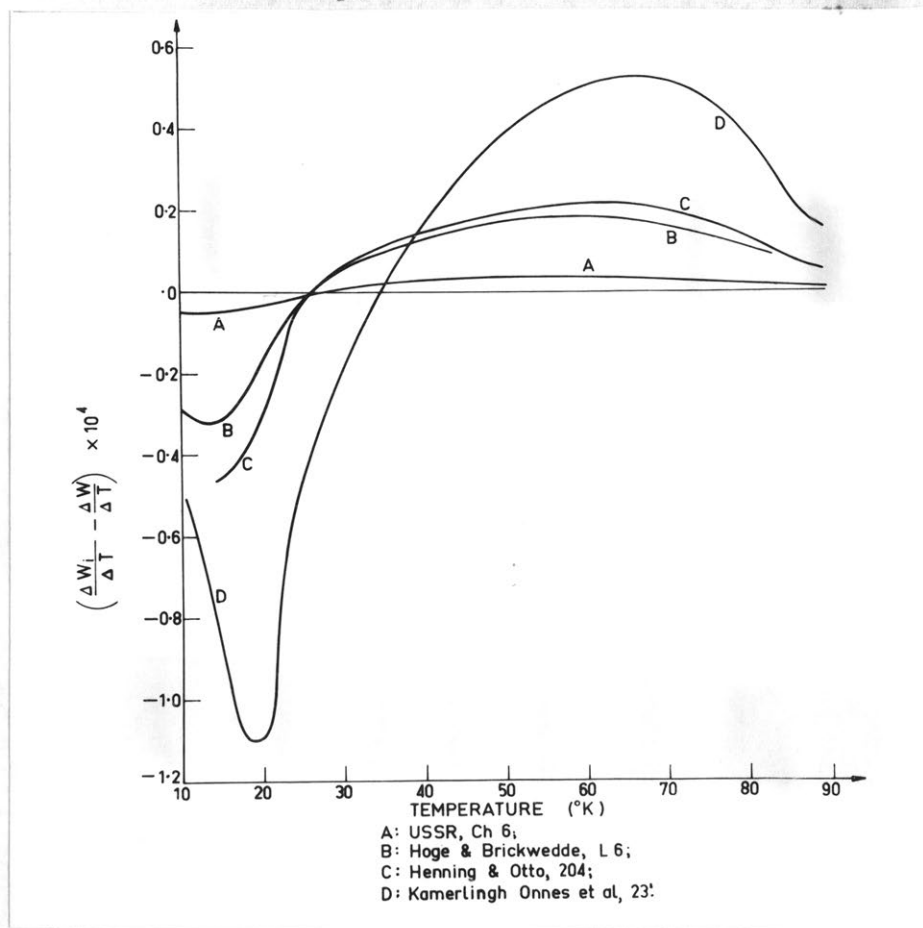


Figure 20. The effect of purity on  $dw/dT$ .

temperature that  $dw/dT$  is relatively most sensitive to changes in the impurity content and this is made more serious by the fact that in this region  $dw/dT$  is already rather small. Thirdly, beginning at the lowest temperatures, where  $dw/dT \rightarrow 0$  for all thermometers, it rises most quickly for the least pure resistors but near  $14^\circ$  the trend reverses until near  $26^\circ$   $dw/dT$  is virtually equal for all reasonably pure elements ( $\alpha > 0.0039$ ). From about  $26^\circ$  to  $56^\circ$  the resistance continues to rise fastest for the purest elements while above this range  $dw/dT$  values converge

again to maintain their relative positions right up to the highest temperatures.

These considerations explain why Los and Morrison's method was successful only to about 20°K (they quite evidently had hoped to use it down to 11°K) and why their calculated and measured differences begin to diverge relatively sharply in this region (see Fig.5) An even sharper divergence would have resulted from the inclusion of thermometers with  $\alpha < 0.003925$ .

On the other hand, use of the Cragoe function between, say, 90° and 30° instead of 90° and 20° should not only result in an improved fit for thermometers of similar purity - this might have been expected in any case - but more important, it should lead to a substantially improved fit for thermometers showing much greater differences in  $\alpha$  than the Los and Morrison instruments. That this is in fact true is illustrated in Table 12 where TS is compared with L6. Since TS was originally calibrated against L6, both instruments should agree to within a few millidegree. Using  $\gamma_{30}$  this is practically achieved while use of  $\gamma_{20}$  leads to increasingly large errors as the critical region of the "cross-over" is approached. It can still be added that it is, of course, evident that a function of the Cragoe type must fail in the range extending from 26° downwards.

Table 12

The Cragoe Function ( $Y_T$ ) for different

Temperature Intervals.

$Y_T(20) = \frac{w_T - w_{20}}{w_{90} - w_{20}}$				$Y_T(30) = \frac{w_T - w_{30}}{w_{90} - w_{30}}$			
Number	TS	L6		Number	TS	L6	
$10^6 a$	.3926	.3917		$10^6 a$	.3926	.3917	
$w_{90} - w_{20}$	.238764	.238203		$w_{90} - w_{30}$	.225867	.225262	
$w_{20}$	.004261	.006513		$w_{30}$	.017158	.019454	
T (°K)	$Y_T(20)$		$\Delta T_{\text{mdg.}}$	T (°K)	$Y_T(30)$		$\Delta T_{\text{mdg.}}$
70	.63761	.63762	0.5	70	.61691	.61680	6
60	.46188	.46195	4	60	.43115	.43104	7
50	.29796	.29812	12	50	.25787	.25779	5
40	.15696	.15724	20	40	.10882	.10882	-

Having made these observations, attention will now be paid to the available calibration results which will be considered in two sections: first, results from  $90^{\circ}$  to about  $27^{\circ}$  and then from  $27^{\circ}$  down to  $14^{\circ}\text{K}$ .

(ii) The Range  $90^{\circ}$  to  $27^{\circ}\text{K}$ .-- The findings described in IV (iv) led to the suggestion of dividing the low temperature range at the triple point of oxygen (Hoge 1950). Arguments in (i)b above, suggest, however, that the dividing line should be drawn just above  $26^{\circ}$  where the normal boiling point of Neon ( $27.07^{\circ}\text{K}$ ) would be available as a fixed point. Both possibilities will now be investigated although the  $27^{\circ}$  limit will have to be tested using published results only for it would not have proved practicable during the present work to carry out measurements in this range to the required degree of accuracy.

It was possible, however, to test the Cragoe function (16) between  $90^{\circ}$  and  $54^{\circ}$  with the results shown in Table 13 where the comparison is extended to four other thermometers calibrated on three different gas thermometer scales. Differences in Y are due mainly to differences in these scales (see IV, iv, and also Hoge and Brickwedde 1939) for where the scales are the same as e.g. for TS and L6 (both PTS) or CT15 and CT18 (both Hoge vapour pressure scale) these differences

Table 13

The Cragoe Function ( $Y_T$ ) for the  
Interval  $90^\circ$  to  $54^\circ\text{K}$ .

Reference	Los and Morrison 1957.	USSR 1954	Hoge and Brickwedde 1939	Henning and Otto 1932	Present Work.		
Number	TS	Ch6	L6	204	CT15	CT18	R10
$10^6 \alpha$	3926	3925	3917	391	3926	3924	3911
$w_{90} - w_{54}$	.15244	.15242	.15206	.15195	.15250	.15243	.15238
$w_{54}$	.09058	.09063	.09266	.09431	.09065	.09106	.09322
$Y_T(54) = \frac{w_T - w_{54}}{w_{90} - w_{54}}$							
85	.85732	.85750	.85717	.85725	.85698	.85698	.85698
80	.71484	.71513	.71471	.71464	.71456	.71456	.71493
75	.57308	.57321	.57294	.57269	.57273	.57273	.57324
70	.43243	.43236	.43233	.43185	.43215	.43215	.42618
65	.29336	.29333	.29324	.29300	.29312	.29313	.29392
60	.15718	.15732	.15710	.15710	.15705	.15713	.15736

are well within  $0.01^{\circ}$  and often less than  $0.001^{\circ}$  notwithstanding some relatively large differences in  $\alpha$  and considerable differences in the origin of the platinum. On the other hand, a thermometer having the  $\alpha - w_{4.2}$  characteristics of R10 (See Figs. 16 and 18B) can hardly be expected to agree with the other instruments and these characteristics are already clearly apparent from a study of the relationships between  $w_{54}$  and  $w_{90}$  which is illustrated in Fig. 21.

If the predictions made in (i) b above could be more generally verified, the Cragoe scale could be used to extend the ITS not only to the triple point of oxygen but even to the normal boiling point of Neon ( $27.07^{\circ}\text{K}$ ) which is just above the critical inversion region shown in Fig. 19.

Table 14 tests this possibility in a more thorough manner than was done in Table 12. This time the results are referred to Ch6 as standard and the instruments listed are the same as those listed in Table 13 with the addition of T4 but excepting the NSL thermometers for they could not be calibrated at  $27^{\circ}$ . Agreement is excellent below  $60^{\circ}$ , T4 being the one exception but then T4 is one of those resistors which does not have a "normal"  $\alpha - w_{4.2}$  relationship (See Fig. 18B and also iii, c, below). At and above  $60^{\circ}$  some of the deviations are noticeably greater. Differences of a similar order were also noted when discussing Table 13 and it was then shown that they

TABLE 14

The Cragoe Function ( $Y_T$ ) for theInterval  $90^\circ$  to  $27^\circ\text{K}$ .

Number	CH6	TS	T4	L6	204	
$w_{90} - w_{27}$	.230978	.230979	.230948	.230371	.230	
$w_{27}$	.012076	.012046	.011986	.014345	.016	
T (°K)	$Y_{\text{Ch6}}$ $\times 10^{+4}$	$\Delta Y^*$ $\times 10^{+4}$	$\Delta T$ mdg	$\Delta Y$ $\times 10^{+4}$	$\Delta T$ mdg	$\Delta Y$ $\times 10$
80	8120.0	2.3	13	1.9	10	3.7
70	6254.0	0.1	1	-0.9	-5	4.5
60	4439.0	1.6	9	0.2	1	3.3
50	2742.8	-0.1	-1	-1.3	-8	0.2
40	1285.1	-0.3	-2	-1.2	-9	0.0
30	221.7	0.3	3	0.0	-	-0.1

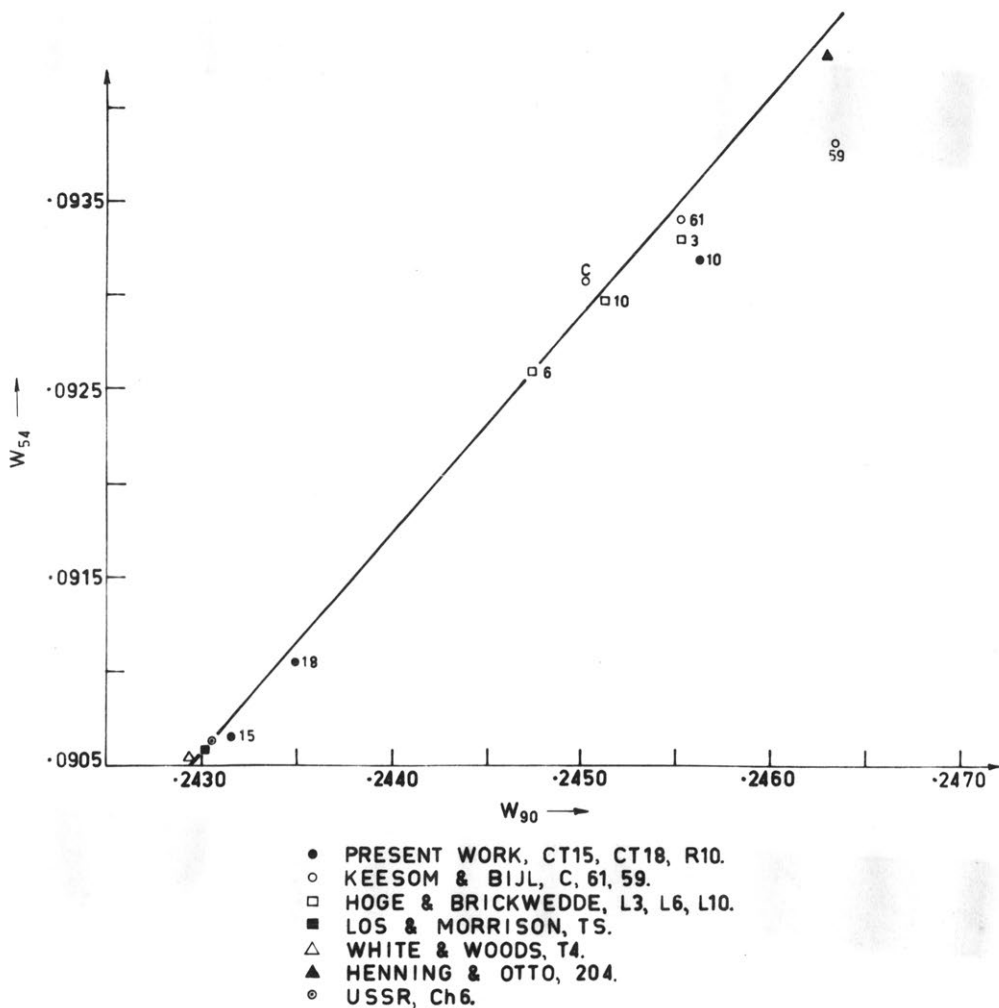


Figure 21.  $w_{54}$  as a function of  $w_{90}$ .  
The straight line is so drawn that it passes through the positions for Ch6 and L6. That CT15 and CT18 are relatively distant from this line is probably due mainly to calibration errors at  $54^\circ$ .



are likely to be mainly the result of differences in the various gas thermometry measurements. That this is also true for the present case is shown once again by the good agreement between TS and L6 which had been noted already in Table 12 and also by the good agreement below  $60^{\circ}$  which should be expected since Fig. 4 shows that the relations between  $w - T$  scales are much smoother in this region than above  $50^{\circ}$ .

It may be added here that an extension of the ITS to at least  $54^{\circ}\text{K}$  should be feasible without much delay. Equation (16) has now been successfully tested over this range for a sufficiently large number of instruments and it would only be necessary therefore to agree on an acceptable  $Y_T$  scale and to fix suitable limits for the ratio  $w_{54}/w_{90}$ . With regard to the experimental procedure for the realisation of the triple point of oxygen it would seem that satisfactory results ought to be attainable by adapting the method suggested by Michels et al. (1957) for the realisation of the triple point of argon, the cooling could be effected in this case by pumping over solid nitrogen which was the device utilised by Lisman and Keesom (1935) for the realisation of the triple point of oxygen.

(iii) The Range  $27^{\circ}$  to  $14^{\circ}\text{K}$ .-- Here as before the limit  $27^{\circ}$  will not be strictly adhered to and this again to make use of the present measurements at  $54^{\circ}\text{K}$ , especially since hardly any of the published data include reliable measurements of  $w_{4.2}$ .



(a) The van der Leeden - Hoge approach. Figures 22 - 24 have been drawn to illustrate the degree of success to be expected from methods such as that suggested by van der Leeden (see IV,iii). This method demands in effect that at any temperature T the ratio  $(w - w_1)_T/z$  should be constant for all thermometers. For the present purpose, ratios were fixed at 15°, 20° and 54° by using

$$\frac{(w_T)_C - (w_T)_{T_4}}{(w_{4.2})_C - (w_{4.2})_{T_4}}$$

thermometer C being chosen because it has the highest published  $w_{4.2}$  value of those resistors for which  $\alpha > 0.00391$  but unfortunately its  $w - T$  table does not go below 15°K. Those ratios, however, fit none of the other instruments and it is in fact clearly impossible to define a ratio such that it would be common or nearly common to more than two of the thermometers shown in Figure 22.

In order to obtain some additional information  $w_{4.2}$  was now calculated for thermometers L3, L6 and L10 using their published  $w_{15}$  values and substituting them in the ratio as defined by Figure 22. Obviously, L6 alone gives a reasonable fit at the other two temperatures, the deviation being equivalent to a few millidegree only. However, a check revealed that these deviations are rather greater between 20° and 54° reaching the equivalent of 0.02° near 30°. This is not surprising in view of the arguments in (i)b above bearing in

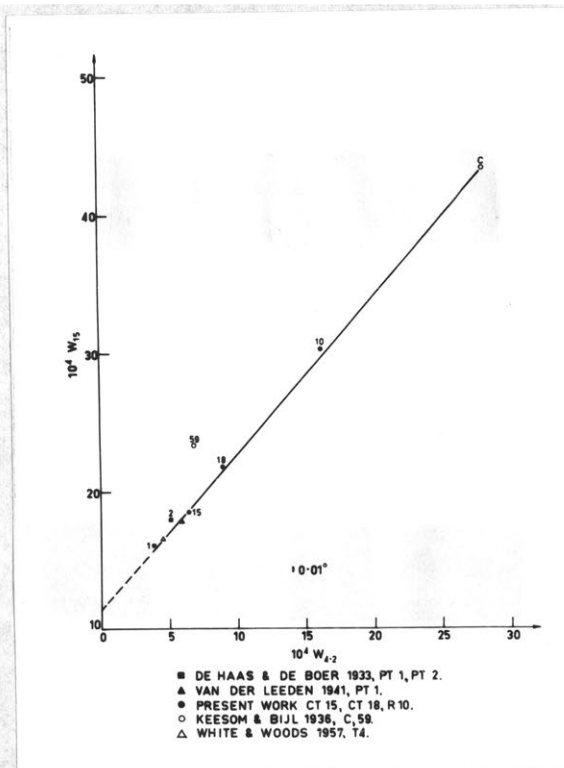


Figure 22.  $w_{15}$  as a function of  $w_{4.2}$

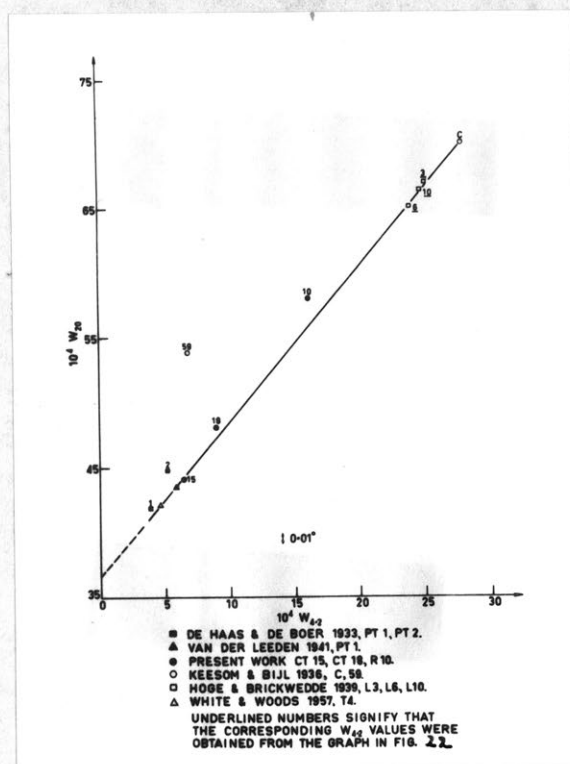


Figure 23.

$w_{20}$  as a function of  $w_{4.2}$

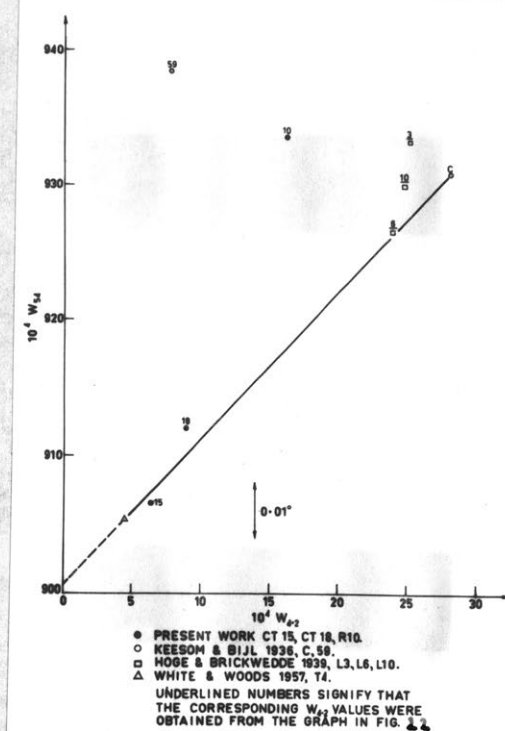


Figure 24.

$w_{54}$  as a function of  $w_{4.2}$

mind that thermometer C has an  $\alpha$  of only 0.003915. The deviations could then be reduced, by excluding thermometers having  $\alpha < 0.003920$ .

Unfortunately, the available data is insufficient to test van der Leeden's method under these restricted conditions for clearly to base the ratio on CT15 and CT18 is useless. An attempt was made to obtain additional data from the N.B.S., Washington, but it met with no response.

Information published by Hoge (1950) is relevant here, however, for Hoge's method is essentially similar to that of van der Leeden's. This was discussed in IV, iii, above when it was also stated that Hoge was able to select seven instruments which after calibration at  $13.813^{\circ}$ ,  $20.273^{\circ}$  and  $54.363^{\circ}$  respectively yielded a common scale within a few millidegree. Although he did not state how many other thermometers failed to fit this scale and by what margin, his advocacy of the method would imply that the number of failures could not have been significantly greater than the number of successes.

Once sufficient thermometers have been calibrated at  $4.2^{\circ}\text{K}$  as well as above  $14^{\circ}$ , it would not be very difficult to discover whether a sufficiently great proportion of them would satisfy the van der Leeden - Hoge method. Algebraically, since for each instrument

$$w_T = w_{4.2} (1 + A_T) \quad (19)$$

$A_T$  which depends on temperature only and is equal to van der Leeden's constant in equation 15, will be given by

$$A_T = \frac{w_T - w_{4.2}^*}{w_{4.2} - w_{4.2}^*} \quad (20)$$

and must be the same for every selected thermometer.

(b) The van Dijk Approach. It is evident from the results of the experimental work reported in Section VI, that deviations from M.R. **cannot** depend only on  $T$  but depend also on  $z$  or even on  $w_i$  and  $z$ . The latter case is implicit in van Dijk's equation 15 and is supported by theory (see III, iv). From the standpoint of standard thermometry it would go too far, however, to allow for all these deviations. Attempts to do so were made during the present work but were abandoned for no methods appeared to be available to determine the necessary corrections in a reasonably convenient and reliable manner.

(c) Thermometers with very high  $\alpha$  values. The refinement of platinum metal has reached such a high standard to-day that wire is readily obtainable having  $\alpha > 0.003925$ . This means, of course, that for such wire residual impurity concentrations are very low and consequently deviations from Matthiessen's Rule closely similar if not identical.

That this is true at least in some cases is shown by the example of CT15 and CT16 (Tables 5 and 10) and also by Los and Morrison's thermometers T1, T2, T3 (Fig.5). It may even be true for CT15 and Ch6 although the difference  $w_{CT15} - w_{Ch6}$  is several times as great as the difference  $w_{CT15} - w_{CT16}$ . There is, however, an element of uncertainty here since CT15 and Ch6 were calibrated with respect to different gas thermometry scales.

On the other hand, Los and Morrison's results also show that deviations from M.R. can differ significantly even for thermometers having  $\alpha > 0.0039255$  (see Fig. 5, T4 and T5). This would not be serious if there were good grounds to believe that the pattern of deviations observed by Los and Morrison would be followed by a large majority of thermometers which may not be true, however, and is certainly not true for CT15 and T4 (see Fig. 16). The different pattern no doubt is due to the fact that while  $\alpha_{TS} > \alpha_{CT15} > \alpha_{T4}$  a comparison between  $w$  values at 18°K ( $w_{TS}$  was not recorded below 18°) showed that at this temperature  $w_{CT15} > w_{TS} > w_{T4}$ .

It is true, however, that in general the changes in the deviations from M.R. take place almost linearly and monotonically over temperature intervals contained within potential calibration points such as the boiling points of neon and hydrogen where  $\Delta w$  could then be evaluated with respect to an agreed standard scale. For example, if the TS scale is chosen as standard and compared with the T4 scale so that  $\Delta w = w_{TS} - w_{T4}$ , then  $\Delta w$  equals  $0.66 \times 10^{-4}$  at 20° and close to  $0.60 \times 10^{-4}$  at 27° and values of  $\Delta w$  obtained by linear interpolation between these figures differ from measured  $\Delta w$  values in this range by at most a little over  $0.01 \times 10^{-4}$  corresponding to at most a little over  $0.001^\circ$ .

Evaluations of  $\Delta w$  on the assumption of linearity between 20° and 27° would then certainly be successful with the Los and Morrison thermometers (see Table 5). Unfortunately, no other suitable  $w - T$  tables are available for trial since Ch6 was calibrated on a different

gas thermometry scale while data for Ctl5 taken from Fig. 16 is not sufficiently reliable other than below 20°.

Since  $w_{TS} - w_{T4}$  reaches a minimum of about  $0.35 \times 10^{-4}$  near 45° K and then rises again to about  $0.4 \times 10^{-4}$  at 54° calibration at 20° and 54° would lead to less accurate interpolation values but even then the error would be small at least on the present case and in terms of temperature differences for at these higher temperatures  $dw/dT$  is also very much greater than nearer 20° (see Fig. 1).

Below 200 this procedure for the evaluation of  $\Delta w$  is less satisfactory because of the increasing smallness of  $dw/dT$  especially since near 15° there occurs another relative shift in the differences between  $dw/dT$  values of thermometers with differing impurity contents (see Fig. 20).

This is not really serious in the present context for a cryostat suitable for thermometer calibration near the boiling point of hydrogen can readily be made to serve for the entire liquid hydrogen range. It would then be most convenient to end the platinum scale at or near the normal boiling point of equilibrium hydrogen (20.273°K) and define the ITS down to the triple point (13.813°K) or possibly even lower in terms of the vapour pressure - temperature relationship of equilibrium hydrogen. A suggestion to this effect already was put forward by the National Bureau of Standards (Procès-Verbaux 1948) and again by Los and Morrison (1951).

It would seem rather pointless to transfer from the vapour pressure thermometer scale to the platinum thermometer scale



when the former is in general more accurately reproducible than the latter and moreover, can be represented by a relatively simple formula (Woolley et al. 1948). The platinum thermometer is, of course, more convenient to use and, therefore, it would be logical to recommend it as the appropriate secondary standard instrument.

The procedures here described should produce an accurately reproducible calibration but there are several qualifications. Firstly, it will be necessary to agree on a standard platinum scale extending from  $90^{\circ}$  down to  $20^{\circ}\text{K}$ . It has been suggested by the *Chambre Centrale des Mesures, U.S.S.R.* (*Proces Verbaux* 1954) that an "ideal" platinum scale should be constructed for such a purpose. Obviously, this can be done only by extrapolation and, therefore, can be undertaken with confidence only in a situation where increases in purity are accompanied by strictly monotonic changes in the property to be extrapolated. So far there is no conclusive evidence for such monotonic changes (see Fig. 18B) and this leaves agreement on a standard scale such as the *Ch6* scale or the *PTS* the only practicable alternative.

Secondly, it would be desirable to use the boiling point of Neon rather than the triple point of oxygen as an intermediate calibration point. The boiling point of Neon would then have to become one of the fundamental fixed points of the *ITS*. Since so far relatively little work has been done on this point (the latest summary which could be found is that by Hoge 1941) it remains to be established that it can be reproduced to a similar order of accuracy as for instance the boiling points of oxygen or of

equilibrium hydrogen and this without unduly greater experimental difficulties.

Thirdly, agreement would have to be attained concerning the equilibrium hydrogen vapour pressure scale. To ensure continuity it might be found advisable to base this vapour pressure - temperature relationship on the same gas thermometry scale used to establish the standard platinum scale.

## VIII. CONCLUSIONS.

The present work leads to the following conclusions:

Extension of the ITS can be relatively most easily accomplished by basing the ITS on a selected Standard Platinum Scale (SPS) since simple and precise procedures are available to relate the platinum scales generated by individual thermometers to the SPS. This contrasts with the procedure adopted above 90°K where the temperatures of a few fixed points only had to be specified.

With regard to limits to the purity of the platinum these limits must be so selected that they not only exclude all thermometers other than those having a specified maximum in their overall impurity concentration, but also all thermometers containing impurities of a kind which would cause their  $w - T$  scales to deviate significantly from the SPS.

At present the most suitable scale for adoption as SPS is that determined at the Chambre Centrale des Mesures, U.R.S.S. (1954). Such a scale, and, therefore, the proposed extension of the ITS, could be reproduced to within a few millidegree (this being similar to the order of reproducibility of the ITS between 90° and 273°K) by adopting for each thermometer ( $w_T$ ) the following procedures:

- (a) with the normal boiling point of oxygen (90.190°K) and the normal boiling point of Neon (27.07°K) as fixed points, the SPS ( $Y_T$ ) could be reproduced using the so-called Cragoe function in the form

$$Y_T = \frac{w_T - w_{27.07}}{w_{90.190} - w_{27.07}}$$

(b) from the normal boiling point of Neon to the normal boiling point of equilibrium hydrogen (20. 273°K) the SPS could be reproduced by determining  $\Delta w = w_T - Y_T$  at these two fixed points whereupon  $\Delta w$  values at temperatures between these points could be obtained by linear interpolation.

The stipulated degree of reproducibility could be achieved only, however, if (1) all calibrated thermometers have  $\alpha/w_{4.2}$  values falling within limits to be specified with due regard to the properties of the SPS. The ratio  $\alpha/w_{4.2}$  could possibly be replaced or just supplemented by  $w_{20}/w_{90}$  which could be determined without the need for an additional calibration point.

(2) with regard to calibrations between 90° and 27°, there is no conclusive evidence so far that present ITS requirements concerning the purity of the platinum must be tightened. Nevertheless, raising the minimum permissible value for  $\alpha$  to 0.003920 should certainly prove a greater safeguard for a satisfactory reproducibility of  $Y_T$  than is the present minimum of 0.003910.

(3) for the range 27.07° to 20.273° satisfactory reproducibility can be ensured only if all thermometers to be calibrated have values within about 1 part in  $10^4$  of the SPS. With the latter based on the scale of the Chambre Centrale des Mesures, U.R.S.S. or a scale determined with a thermometer of similarly high purity as the Russian instrument Ch6, this requirement could be most safely satisfied by stipulating that instruments to be calibrated should have  $\alpha > 0.003925$ , although the question of an upper limit to  $\alpha$  may have to be considered in due course.

It is concluded that using the procedures here described, the SPS is sufficiently easily and accurately reproducible to justify its use for the extension of the ITS down to 20°K.

Below 20° a scale based on the vapour pressure-temperature relationship of equilibrium hydrogen can be reproduced more accurately than a platinum resistance scale. Moreover, this vapour pressure-temperature relation can also be more conveniently formulated than the  $w - T$  relation. Consequently, the SPS should be ended near 20° and the ITS could then be based on an equilibrium hydrogen vapour pressure scale which could extend down to the triple point (13.813°K) or even a few degrees lower. To ensure precise continuity with the SPS it would be advisable to base the vapour pressure scale on the same gas thermometry scale as the SPS. The platinum resistance thermometer could, of course, be recommended as a suitable secondary standard instrument certainly down to 14°K and it would then stand in a somewhat similar relation to the vapour pressure thermometer as does the mercury-in-glass thermometer to the platinum thermometer in the range - 35° to about 400°C.

To obtain at least some improvement over the present situation and this with as little delay as possible, the ITS could be extended in the first instance to the well-established temperature of the triple point of oxygen (54.363°K). For this purpose only that part of the proposed SPS is required which can

be reproduced by the thoroughly tested relation

$$Y_T = \frac{w_T - w_{54.363}}{w_{90.190} - w_{54.363}}$$

A  $Y_T$  scale for this range could be defined for instance by a combination of the Provisional Temperature Scale of the NBS and the Russian scale. It should again be advisable to specify  $\alpha > 0.003920$  and furthermore, definite limits should be fixed for the ratio  $w_{90.190}/w_{54.363}$  to exclude thermometers which develop irregularities in their  $w - T$  scales only below  $90^\circ\text{K}$ .

## IX. ACKNOWLEDGMENTS.

The author is foremostly indebted to the Chief, Division of Physics, National Standards Laboratory, C.S.I.R.O. (Dr. G. H. Briggs) and to Mr. A. F. A. Harper, Head of the Heat Section in this Division, for helpfully making available to him the facilities of the Division for the present project, and for recommending him for a generous grant paid by the C.S.I.R.O. Mr. Harper, as immediate supervisor, moreover gave encouraging assistance and many valuable suggestions through the entire period.

The author also gratefully acknowledges the co-operative attitude of the Head of the School of Applied Physics, N.S.W. University of Technology (Professor C. J. Milner) and of Mr. C. E. Curnow, who acted as supervisor representing the University.

It is a particularly pleasant duty to acknowledge the help received throughout from Mr. W. R. G. Kemp, of the Division of Physics whose contribution to this work could hardly be overestimated. His part in the design of the apparatus has already been referred to, he also supervised its operation and took part in all readings. The author came to Sydney wholly ignorant of the complicated techniques of low temperature work and what knowledge he has acquired on this subject is almost entirely the result of Mr. Kemp's instruction and advice.

Concerning the part of the work dealing with the theory of electrical conduction in platinum, the author had many most helpful discussions with Dr. P. G. Klemens of the Division of

Physics who, moreover, kindly contributed the interpretations and suggestions given in the last part of Section III above.

The author found throughout his work a spirit of willing co-operation and readiness to give assistance whenever required on the side of all members of the staff of the Division of Physics, including that of the drawing office. Special mention in this connection is due to Messrs. J. A. Birch, G. E. Nightingale, and J. W. Smyth, who gave welcome and valuable help on numerous occasions.

Finally thanks are due to the Chief Superintendent, Defence Standards Laboratories, Maribyrnong, Victoria, for making available one of the resistance thermometers (D1) used during this work.



## A P P E N D I X 1.

### THE PARA AND ORTHO MODIFICATIONS OF HYDROGEN AND THEIR EFFECT ON PRECISION THERMOMETRY IN THE HYDROGEN RANGE.

(i) Introduction.-- Molecular hydrogen is not a homogeneous gas but a mixture of two species known respectively as para-hydrogen ( $p\text{-H}_2$ ) and ortho-hydrogen ( $o\text{-H}_2$ ). Although the ratio between these two modifications (when in thermodynamic equilibrium) is a single valued function of the temperature, any given mixture can exist for long periods (compared to the time taken for most experimental work) in a metastable state at very much lower (or higher) temperatures. Since the two species differ in many important physical properties, including their vapour pressures (see Fig.A1) this just mentioned characteristic of hydrogen is of considerable significance to low temperature thermometry and in particular to the present project which is based on the temperature scale defined by the Vapour Pressure - Temperature relationship of equilibrium hydrogen.

(ii) Theory.-- The existence of molecules of para- and ortho-hydrogen was first inferred from quantum mechanical reasoning by analogy with helium atoms: the spin properties of the electrons of the helium atom being paralleled by those of the protons of the hydrogen molecule. These spin properties lead to two distinct states: parallel spins leading to the ortho states and anti-parallel spins to the para states. Since each proton has a spin

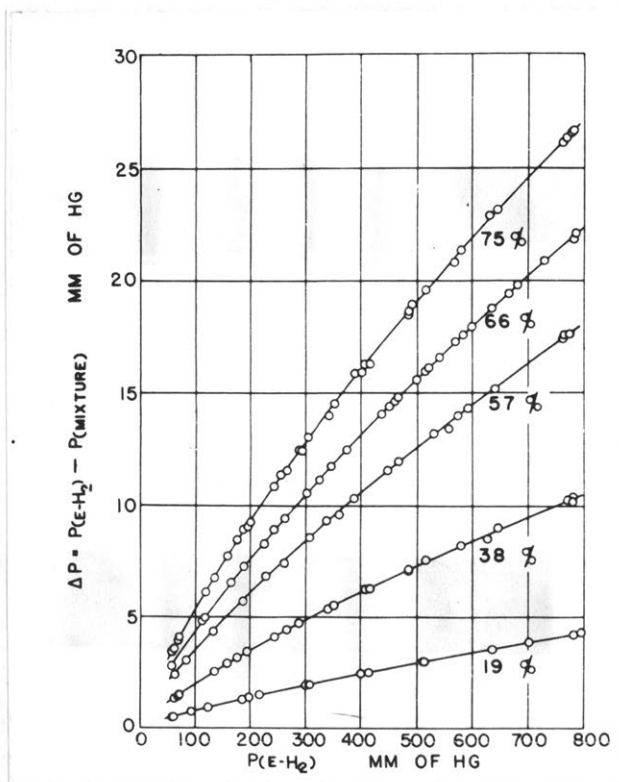


Figure A1. Changes in the vapour pressure of equilibrium hydrogen (E-H<sub>2</sub>) due to contamination with ortho-hydrogen (after Wooley et al. 1948).

of half a unit ( $\frac{1}{2}h/2\pi$ ), the total spin in the former case will be unity and zero in the latter case. Moreover, since the states of antiparallel spin are represented by the symmetrical solutions of the Schrodinger equation for the molecule, such molecules have even rotational quantum numbers ( $J=0, 2, 4...$ ) the states of parallel spin, on the other hand, are represented by the antisymmetrical solutions so that the corresponding molecules have odd rotational quantum numbers ( $J=1, 3...$ ). As the temperature falls the molecules must pass into the para states which include the state  $J=0$ .

At any temperature  $T$  the thermodynamic equilibrium for each state is given by the Boltzmann distribution law

$$N_J = N_0 P_J e^{-E(J)/kT}$$

where  $N_J$  is the fraction of  $N_0$  molecules in the state  $J$ ,  $E(J)$  the energy of this state and  $P_J$  its statistical weight. If the  $p\text{-H}_2$  and  $o\text{-H}_2$  molecules have concentrations  $C_p$  and  $C_o$  respectively, then, in equilibrium

$$\frac{C_p}{C_o} = \frac{\sum_{J \text{ even}} P_J e^{-E(J)/kT}}{\sum_{J \text{ odd}} P_J e^{-E(J)/kT}}$$

The graph in Fig. A2 shows the value of this ratio (expressed as the percentage content of  $p\text{-H}_2$ ) as a function of the temperature. However, thermodynamic equilibrium distributions below room temperature can be attained with reasonable speed only in the presence of suitable catalysts which means that the transition  $\Delta J = \pm 1$  is ordinarily prohibited (Dennison 1927). It is this characteristic of the mixture which is responsible for complications during low temperature vapour pressure measurements.

Experimental evidence for the existence of the two species was first published in 1929 by Bonhoeffer and Harteck (Farkas 1935; this book, which is still the standard reference on the subject of hydrogen modifications, will hereafter be referred to as "Farkas"). This evidence furnished a striking

confirmation of the correctness of quantum theory.

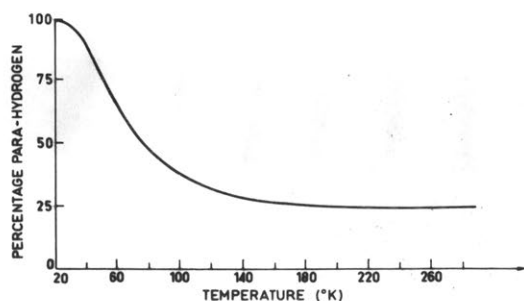


Figure A2. The p-H<sub>2</sub> concentration in hydrogen as a function of Temperature.

**iii. Ortho-Para Transitions.**- (a) Spontaneous transitions. Although the transition  $\Delta J = \pm 1$  is nominally prohibited, this prohibition is really effective only in the gas phase (and at moderate pressures) where the half-life time of a mixture subject to non-catalysed ortho-para conversions is of the order of three years. These rare conversions are brought about by (1) direct transitions between the two levels caused by internal radiation, (2) collisions with other hydrogen atoms or molecules, (3) spin reversals due to the interaction of the magnetic moments of the protons and molecules (Amphlett 1947).

Gaseous mixtures of the two species are virtually stable therefore even if their p-H<sub>2</sub> concentration is not in equilibrium at the given temperature of the gas. In particular, the room temperature mixture which contains 25 per cent. p - H<sub>2</sub> (see Fig.A2)

and is commonly known as normal hydrogen ( $n\text{-H}_2$ ) is stable for the purpose of most experimental work at lower temperatures. These facts led to many difficulties until Dennison recognised their origin (see A. Farkas, pp.33/34).

The frequency of occurrence of processes (2) and (3) above, increases markedly with particle density. Therefore, the rate of conversion is enormously accelerated after condensation (Gremer and Polanyi 1933). Keesom et al. (1931) found that the boiling point of hydrogen decreased at an average rate of about  $0.0008^\circ\text{C}$  per hour so that the  $p\text{-H}_2$  concentration must increase by about 0.5 per cent. per hour. (As shown in Table A1, the boiling points of normal and equilibrium hydrogen differ by about  $0.12^\circ\text{K}$ ) It follows that high precision in hydrogen vapour pressure thermometry cannot be realised unless the stability (and composition) of the liquid in the vapour pressure thermometer bulb has been ensured by first catalysing the normal hydrogen to the equilibrium mixture for the liquid state (99.8 per cent  $p\text{-H}_2$ ).

It must still be mentioned that  $20^\circ\text{K}$  equilibrium hydrogen ( $e\text{-H}_2$ ) at room temperature is far less stable than gaseous normal hydrogen near  $20^\circ\text{K}$ , the probability of a para-ortho conversion being about three times larger than that of the reverse reaction (A. Farkas, p.66). This means that  $20^\circ\text{K}$   $e\text{-H}_2$  stored at room temperature must be used within a few weeks after preparation if the  $p\text{-H}_2$  content is not to fall much below 99 per cent. During storage the gas must be carefully protected from moisture and paramagnetic substances (see below).

Table Al. Boiling Points and Triple Points of the  
Hydrogen Modifications (from Wooley et al. 1948)

Modification	Temp. °K.	Point or State	Vap. Press. mm. Hg.
n - H <sub>2</sub>	20.39	boiling	760
e - H <sub>2</sub>	20.39	liquid	787
e - H <sub>2</sub>	20.27	boiling	760
n - H <sub>2</sub>	13.96	triple	54.0
e - H <sub>2</sub>	13.96	liquid	57.4
e - H <sub>2</sub>	13.81	triple	52.8

(b) Catalysed transitions. The conversion process can be very much accelerated by the use of suitable catalysts. Such catalysts must have two specific properties. Firstly, they must be good absorbers of hydrogen for the molecules of the absorbed gas will then be relatively closely packed in the surface layers of the catalyst which facilitates the interchange of atoms as well as magnetic interactions. Secondly, the surface of a good catalyst should also be paramagnetic for the perturbations caused by the extremely inhomogenous magnetic fields of the paramagnetic molecules or ions have the effect of partially removing the transition prohibition (A Farkas, p.79). The catalytic efficiency of charcoal at low temperatures is due largely to its excellent adsorbtivity although its surface is also slightly paramagnetic (Taylor and Sherman 1932)



Paramagnetic substances like magnetite ( $\text{Fe}_3\text{O}_4$ ) which are not good adsorbents or good adsorbents which are diamagnetic as lanthanum oxide ( $\text{La}_2\text{O}_3$ ) are far less efficient. On the other hand, neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) used for the present work, which is a good adsorber as well as strongly paramagnetic is a considerably better catalyst than charcoal (Taylor and Diamond 1933 and 1935).

More recently very efficient catalysts have been developed by the Cryogenic Engineering Department of the National Bureau of Standards (Grilly 1953b) which are now available commercially. The substances used consist of chromium and aluminium oxides. This work was prompted mainly by the desire to reduce evaporation losses when storing liquid hydrogen (Larsen et al. 1948), the losses being due to the liberation of the heat of conversion (see below).

(iv) The Measurement of the Para Content of Hydrogen.-- The progress of conversion from normal to equilibrium hydrogen is most conveniently checked by thermal conductivity measurements since for constant mass and viscosity (as given in this case) the ratio between the thermal conductivities of two gases is proportional to that between their specific heats at constant volume. In this case the specific heat of para hydrogen is markedly higher than that of ortho hydrogen, the difference reaching a maximum between 160° and 180°K. Using the Schleiermacher hot wire method with the cell submersed in liquid nitrogen, Bonhoeffer and Harteck (1929) showed experimentally that in these conditions the resistance change of a platinum wire

heated by a constant current happens to be almost exactly proportional to the change of the  $p\text{-H}_2$  content of the hydrogen in the cell. Measurements with normal hydrogen in the cell and with a second known mixture are sufficient, therefore, to calibrate such a gauge for the entire range of  $p\text{-H}_2$  concentrations. By operating the wire between 1600 and 1800°K the sensitivity of the method is such that resistance measurements to 1 part in 1000 are sufficient to determine the  $p\text{-H}_2$  content of the hydrogen sample in the cell to 1 per cent.

Grilly (1953a) suggested a modification in this method by connecting two cells (matched Pirani gauge tubes) into opposite arms of a Wheatstone bridge circuit and measuring the out-of-balance current for a constant bridge current as the  $p\text{-H}_2$  content in one of the cells is increased; the other cell remaining filled with  $n\text{-H}_2$ . He too submerged his cells into liquid nitrogen to keep the temperature of their walls constant and filled them to a pressure of 40 mm of mercury for at this level pressure changes up to  $\pm 1$  mm have no noticeable effect on the out-of-balance current.

Because of its simplicity, Grilly's method has been adopted for this present work (see V(iii) A above) although it suffers from the disadvantage of non-linearity. The reason for this is likely to be two-fold; firstly, the resistance of the hot wire in the para enriched cell changes by more than 5 per cent. for the total range of  $p\text{-H}_2$  changes. But since, the bridge current is constant, the potential drop across the bridge must vary



accordingly which, in turn, will affect the out-of-balance current. Secondly, the decrease in the resistance of the bridge arm containing the cell with the para-hydrogen (which has the higher thermal conductivity) increases the current in this arm and thereby its temperature and once this temperature exceeds 180°K, the sensitivity of the apparatus will decrease (see above). This last named effect could be reduced, of course, by an appropriate reduction of the working current but this could require the use of more sensitive meters and so detract from the simplicity of the apparatus without gaining complete linearity because of the continued operation of the first named effect.

The cells are calibrated by catalysing hydrogen near 77°K (50 per cent. p-H<sub>2</sub>) in a charcoal trap cooled by liquid nitrogen (3 in Fig. 10) and near 20°K (99.8 per cent. p-H<sub>2</sub>) in the neodymium oxide tube situated in the cryostat (13 in Fig. 12). The normal hydrogen is drawn from a 2000 ml storage bulb (4 in Fig. 10). Before every reading the bridge zero is checked by filling both cells with normal hydrogen. The calibration curve is reproduced in Fig. A3.

An idea of the difference in the conversion efficiencies of the two catalysts is given in Fig. A4, where the progress of conversion on each of them is shown as a function of time. Although for the given experimental set-up the conditions for conversion are more favourable in the charcoal trap than in the Nd<sub>2</sub>O<sub>3</sub> tube, the velocity constant  $k$  for the conversion on charcoal is less than 15 per cent. of that on Nd<sub>2</sub>O<sub>3</sub> where  $k$  is defined by the equation

$$p_t - p_{\infty} = (p_0 - p_{\infty}) e^{-kt}$$

$p_0$ ,  $p_t$ ,  $p_{\infty}$  being respectively the  $p\text{-H}_2$  concentrations at the beginning of the reaction, after a time  $t$  and at the end of the reaction, i.e. on reaching equilibrium.

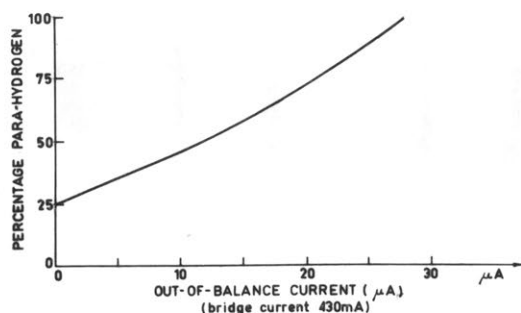


Figure A3. Calibration curve for the Grilly cells.

Before proceeding to the use of a catalyst several precautions have to be observed. Catalysts such as charcoal and neodymium oxide must be thoroughly baked in vacuum. For the present work they were baked at about  $440^{\circ}\text{C}$  for some 6 hours. To keep the surface of the catalysts "clean", they are then maintained in an atmosphere of hydrogen which has been carefully purified particularly from traces of oxygen and moisture. Oxygen is a paramagnetic gas and as such, in proper circumstances, an aid to conversion. However, if admitted into the system at temperatures much above  $90^{\circ}\text{K}$  it will react with most catalysts and so lessen their effectiveness (Bonhoeffer et al. 1933).

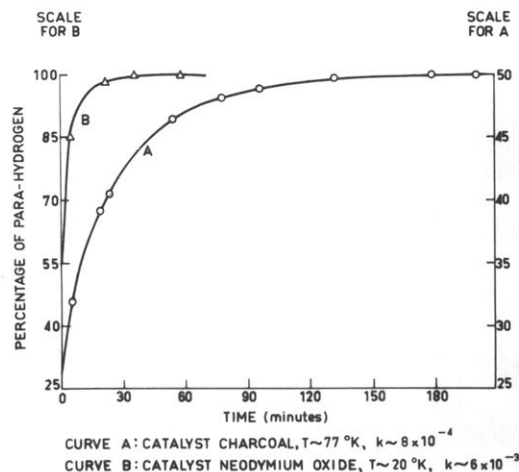


Figure A4. Conversion rates on charcoal and  $\text{Nd}_2\text{O}_3$ .

Finally, during the progress of a conversion, steps must be taken to absorb the resulting heat which, for a complete change from  $n\text{-H}_2$  to  $20^\circ\text{K } e\text{-H}_2$  amounts to over 320 cal/mole (Giauque 1930). Hence, the neodymium oxide tube in the cryostat must remain below the liquid hydrogen surface during the progress of the conversion, otherwise the liberated heat may raise the temperature of the catalyst above  $20^\circ\text{K}$  which would result in a decrease of the  $p\text{-H}_2$  content of the hydrogen (see Fig. A2).

## R E F E R E N C E S

(The subject matter of the papers has been indicated in some of the cases. )

- AMPHLETT, C.B. (1947).- "Ortho- and Para-Hydrogen." National Research Council of Canada, Report No. 1680.
- ASTON, J.G. (1941).- "Copper-Constantan Thermocouples at Temperatures down to 11°K." in "Temperature" Vol. 1 p.219, Reinhold Publ. Corp. New York.
- ASTON, J.G. and MOESSEN, G.W. (1953).- J. Chem. Phys. 21:948.
- ASTON, J.G., WILLIHNGANZ, E. and MESSERLY, G.H. (1935). - "The copper-constant thermocouple from 12° to 273°K". J. Am. Chem. Soc. 57:1642.
- BABER, W.G. (1937). - "Resistance in metals due to collisions between electrons". Proc. Roy. Soc. (London) A 158:383.
- BARBER, C.R. (1955).- "A low temperature platinum resistance thermometer". J.Sci. Instrum. 32:416.
- BENEDEK, G.C. and KUSHIDA, T. (1957).- Rev. Sci. Instrum. 28:92.
- BLOCH, F. (1930). - "The electrical resistance law at low temperatures." Z.f.Phys. 59:208.
- BONHOEFFER, K.F., FARKAS, A. and HUMMEL, K.W. (1933).- Z.Phys. Chem. 21B:225.
- BONHOEFFER, K.F. and HARTEK, P. (1929).- Z.Phys. Chem., 4B:113.
- BROOM, R.F. and ROSE-INNES, A.C. (1956).- "Simple equipment for a low temperature laboratory." J. Sci.Instrum. 33:420.
- CATH, P.G., ONNES, H.K. and BURGERS, J.M. (1917).- "Comparison of platinum and gold resistance thermometers with the helium gas thermometer." Leiden Comm. 152c.
- CHAMBRE CENTRALE DES MESURES, U.R.S.S.(1954).- "Memorandum on the extension of the ITS below 90°K." Proces Verbaux 24:T141.
- CREMER, E. and POLANYI, M. (1933).- "Kinetics of ortho-para transitions." Z.Phys. Chem. 21B:459.

- DAUPHINEE, T.M., MacDONALD, D.K.C. and PEARSON, W.B. (1953).-  
"Copper v. copper 0.005 w.t.% tin thermocouples in  
the range 2° to 30°K." J. Sci. Instrum. 30:399.
- DeHAAS, W.J. and deBOER, J. (1933).- "Electrical resistance of  
platinum at low temperatures." Leiden Comm. No. 231 c.
- DENNISON, D.M. (1927). - "The specific heat of the hydrogen  
molecule". Proc. Roy. Soc. A115:483.
- EPPLEY, M. (1932).- "Modifications to Mueller bridge". Rev. Sci.  
Instrum. 3:687.
- FARKAS, A. (1935).- "Ortho-Hydrogen, Para-Hydrogen, and Heavy  
Hydrogen." Cambridge University Press.
- GIAUQUE, W.F. (1930).- J. Am. Chem. Soc. 52:4808, 4816.
- GIAUQUE, W.F. (1947).- "Use of pyrex glass dewars etc. at liquid  
helium temperatures." Rev. Sci. Instrum. 18:852.
- GIAUQUE, W.F., BUFFINGTON, R.M. and SCHULZE, W.A. (1927).- "Copper-  
Constantan thermocouples and the hydrogen thermometer  
compared from 15° to 283°K." J. Am. Chem. Soc. 49:2343.
- GRILLY, E.R. (1953a).- Rev. Sci. Instrum. 24:72.
- GRILLY, E.R. (1953b).- Rev. Sci. Instrum. 24:899.
- GRUNEISEN, E. (1930).- "A new formula for electric resistance."  
Leipziger Vortrage p.46.
- GRUNEISEN, E. (1933).- "The temperature dependence of the  
electrical resistance of pure metals." Ann. d. Physik (5)  
16:530.
- HENNING, F. (1913).- "Comparison between the hydrogen thermometer  
and resistance thermometers from 0° to - 193°K." Ann. d.  
Physik (4), 40:635.
- HENNING, F. (1928).- "A new formula for platinum resistance  
thermometry between 90° and 20°K." Naturwiss. 16:617.
- HENNING, F. and OTTO, J. (1932).- "Calibration of PTR 204".  
Zeitschr. f.d.ges.Kalte-Ind. 39:86.
- HENNING, F. and OTTO, J. (1932a).- "An interpolation formula  
for resistance thermometry." Zeitschr. f.d.ges. Kalte-  
Ind. 39:86..



- HENNING, F. and OTTO, J. (1936a).- "Calibration of PTR 205." Phys. Z., 37:601.
- HENNING, F. and OTTO, J. (1936b).- "The platinum resistance thermometer as temperature standard between 14° and 90°K Phys. Z., 37:639.
- HENNING, F. and OTTO, J. (1936c).- "Vapour pressure curves between 14° and 90°K. Phys. Z., 37:633.
- HOGE, J.H. (1941).- "A practical temperature scale below 90°K" in "Temperature. Its Measurement and Control in Science and Industry". Vol. 1, p.141, Reinhold Publ. Corp., New York.
- HOGE, J.H. (1950).- "An R-T relation for low temperature thermometry." Rev. Sci. Instrum., 21:815.
- HOGE, J.H. (1950a).- J. Research, NBS, 44:321, RP 2081.
- HOGE, J.H. and ARNOLD, R.D. (1951).- J. Research NBS, 47:63, RP 2228.
- HOGE, J.H. and BRICKWEDDE, F.G. (1939).- "Establishment of a temperature scale for the calibration of thermometers between 14° and 83°K." J. Research NBS, 22:351, RP 1188.
- HOGE, J.H. and BRICKWEDDE, F.G. (1942).- "Intercomparison of platinum resistance thermometers between - 190° and 445°C." J. Research NBS, 28:217, RP 1454.
- JEFFREYS, H. (1937).- "Scientific Inference." Cambridge University Press.
- KEESOM, W.H. (1939). - "Comments on the ITS." Proces-Verbaux, 19:T105.
- KEESOM, W.H. and BIJL, A. (1936).- "Comparison of platinum resistance thermometers with the helium thermometer from - 190° to -258°C." Leiden Comm. No. 242 b.
- KEESOM, W.H., BIJL, A. and v.d. HORST, H. (1931).- "Vapour pressures of normal and para hydrogen." Leiden Comm. No. 217a.
- KEESOM, W.H. and LISMAN, J.H.C. (1935).- "The melting curve of oxygen." Leiden Comm. No. 239a.

- KEMP, W.R.G., KLEMMENS, P.G., SREEDHAR, A.K. and WHITE, G.K. (1955).-  
"Thermal and electrical conductivity of palladium at low  
temperatures." Phil. Mag. 46:811.
- KEYES, F.G. (1941).- "Gas thermometer scale corrections", in  
"Temperature", Vol. 1, p. 45, Reinhold Publ. Corp.  
New York.
- KRANTZ, E. and SCHULTZ, H. (1957).- "Deviations from Matthiessen's  
rule for gold and silver." Z. f. Naturforschung, 12a:710.
- KUNZLER, J.E., GEBALLE, T.H. and HULL, G.W. (1957).- Rev. Sci.  
Instrum. 28:96.
- LARSEN, A.H., SIMON, F.E. and SWENSON, C.A. (1948).- Rev. Sci.  
Instrum. 19:266.
- LINDNER, C.T. (1950).- "The measurement of Low Temperatures."  
Westinghouse Research Laboratories, Report R-94433-2-A.  
Pittsburgh, Penn.
- LOS, J.M. and MORRISON, J.A. (1951).- "Calibration of platinum  
resistance thermometers between 11° and 90°K." Canadian  
J. Phys. 29:142.
- MacDONALD, D.K.C. (1956).- "Electrical Conduction of Metals and  
Alloys at low Temperatures." in "Handbuch der Physik,  
Vol. 14, pp. 137/197, Springer Verlag, Berlin.
- McLAREN, E.H. (1957).- "Precision measurements with platinum  
resistance thermometers." Canadian J. Phys. 35:78.
- MATTHIESSEN, A. and VOGT, C. (1864).- "A rule for the temperature  
co-efficient of electrical resistance for alloys."  
Pogg. Ann., 116:369.
- MEISSNER, W. (1935).- "Handbuch der Experimentalphysik", Vol. 11,  
Part 2, Ch. 2 Akad. Verlagsges. m.b.H., Leipzig.
- MEYERS, C.H. (1932).- J. Research NBS, 9:807, R.P.508.
- MICHELS, A., WASSENAAR, T., SLUYTERS, Th. and de GRAAF, W. (1957).-  
The triple points of carbon dioxide and argon as fixed  
points for the calibration of thermometers." Physica  
23:89.

- MOSER, H. (1930).- "Platinum thermometers to 1100°C." Ann. d. Phys. (5), 6:852.
- MOTT, N.F. and JONES, H. (1936).- "The Theory of the Properties of Metals and Alloys." Clarendon Press, Oxford.
- NATIONAL BUREAU OF STANDARDS MEMORANDUM (1948).- Proces Verbaux 21: T84.
- MERNST, W. (1911).- Ann. d. Phys. (4) 36:395.
- ONNES, H.K. and CLAY, J. (1906).- "The resistance of platinum at hydrogen temperatures." Leiden Comm. No. 107c.
- ONNES, H.K. and TUYN, W. (1926).- "Electrical resistance of elementary substances below - 80°C." Leiden Comm. 180 Suppl. 58.
- PILIPTCHONK, B.I. (1954).- "Platinum resistance thermometers between 0° and 1063°C." Proces-Verbaux 24:T134.
- PINES, D. (1956).- "Electron interaction in solids." Canadian J. Phys. 34:1379.
- QUINNELL, E.H. and FUTCH, A.H. (1950).- Rev. Sci. Instrum. 21:400.
- RAYNE, J.A. (1957).- "Heat capacity of palladium below 4.2°K." Phys. Rev. 107:669.
- RAYNOR, G.V. (1952).- "Band structure of transition metals." (p.221 ff) Reports on Progress in Physics, Vol. 15.
- SCHULTZ, H. (1957).- "Deviations from Matthiessen's rule for platinum resistance thermometers between 20° and 90°K." Z. f. angew. Physik, 9:465.
- SCOTT, R.B. (1955).- "Low Temperature Scales from 90° to 5°K." in "Temperature", Vol. 2, p.179.
- SONDHEIMER, E.H. (1950).- "Transport phenomena in metals." Proc. Roy. Soc. A203:75.
- SONDHEIMER, E.H. and WILSON, A.H. (1947).- "The theory of the magneto-resistance effects in metals." Proc. Roy. Soc. A190:435.



- SOUTHARD, J.C. and MILNER, R.T. (1933).-- "Calibration of platinum thermometers with the helium gas thermometer between 14° and 110°K." J. Am. Chem.Soc. 55,;4384.
- STIMSON, H.F. (1952).-- "Constants in the ITS interpolation formulae for resistance thermometers." Proces-Verbaux, 23B:T104.
- STIMSON, H.F. (1955).-- "Precision Resistance Thermometry" in "Temperature", Vol. 2, p.141, Reinhold Publ. Corp. New York.
- STULL, D.R. (1949).-- Chem. Eng. News 27:2772.
- SUDOVTSOV, A.I. and SEMENENKO, E.E. (1957).-- "Temperature dependence of the resistance of platinum between 4.2° and 1.2°K." Soviet Physics, JETP, 4:592.
- SWANSON, C.A. and STAHL, R.H. (1954).-- "A cryostat for producing temperatures between 4° and 80 K." Rev. Sci. Instrum. 25:608.
- Van Der LEEDEN, P/ (1941).-- "Thesis on the conduction of heat and electricity in metals." Leiden University.
- Van DIJK, H. (1952).-- "Use of the platinum resistance thermometer for measuring low temperatures." Proces-Verbaux, 23B:T48.
- Van DUSEN, M.S. (1925).-- "Platinum resistance thermometry at low temperatures." J. Am. Chem. Soc. 47:326.
- WHITE, G.K. and WOODS, S.B. (1957).-- Rev. Sci. Instrum. 28:638.
- WHITE, G.K. and WOODS, S.B. (1957a).-- "Thermal and electrical conductivity of rhodium, iridium and platinum." Canadian J. Phys., 35:248.
- WILSON, A.H. (1953).-- "The Theory of Metals", 2nd Edition Cambridge University Press.
- WOOLLEY, H.W., SCOTT, R.B. and BRICKWEDDE, F.G. (1948).-- J. Research NBS. 41:379, R.P. 1932.
- ZEMANSKY, M.W. (1957).-- "Heat and Thermodynamics". 4th Edition. McGraw-Hill Book Comp. Inc., New York.

.....

# A simple calibration technique for improving the accuracy of a Smith resistance thermometry bridge

By G. C. LOWENTHAL, B.A., B.Sc., A.Inst.P., Defence Standards Laboratories, Department of Supply, Melbourne, Australia

[Paper received 23 November, 1956]

The Smith resistance thermometry bridge (type 3) used at Defence Standards Laboratories is subject to irregular drifts which cause errors exceeding  $\pm 0.002^\circ \text{C}$  between 0 and  $100^\circ \text{C}$  and  $\pm 0.01^\circ \text{C}$  at  $630^\circ \text{C}$ . These errors cannot be dealt with successfully by potentiometric calibrations. An analysis shows, however, that provided certain conditions are satisfied, an external decade of stable  $10 \Omega$  resistors can be used to reduce the errors to  $\pm 0.0005$  and  $\pm 0.001^\circ \text{C}$  respectively, since the calibration is sufficiently simple and quick to be repeated as often as required.

A platinum resistance thermometer having the resistance  $R_T$  at a temperature  $T$  and the resistances  $R_0$  and  $R_{100}$  at the freezing and boiling points of water respectively, defines a so-called platinum temperature  $T_{Pt}$  in accordance with the relation

$$T_{Pt} = \frac{100(R_T - R_0)}{R_{100} - R_0} \quad (1)$$

$T_{Pt}$  is corrected to International Temperature  $T$  by means of the Callendar equation

$$T = T_{Pt} + \delta \left( \frac{T}{100} \right) \left( \frac{T - 100}{100} \right) \quad (2)$$

the value of the constant  $\delta$  being determined by a thermometer calibration at the boiling point of sulphur.

Obviously, only  $T_{Pt}$  as defined by (1) is affected directly by errors in resistance measurements and because of the form of (1) the effect of such errors will vanish, provided they are (a) the same for every resistance reading, or (b) proportional to every resistance reading. In addition they must be reproducible during a thermometer calibration and subsequent series of temperature measurements. The resistance bridge must, therefore, be free from drifts or fluctuations during a time interval sufficiently long to cover these measurements, or means must be available to measure these fluctuations so that they can be allowed for in any subsequent calculations of temperature.

## ERRORS ARISING FROM THE SMITH BRIDGE BALANCE EQUATION

The circuit diagram of the type 3 Smith bridge<sup>(1)</sup> is given in Fig. 1(a) and reference to this figure will explain the symbols used in the analysis below. Its balance equation is

$$P = \frac{R}{S}(Q + L_3) + \frac{bL_2}{a + b + L_1 + L_2} \left( \frac{Q + L_3}{S} - \frac{a + L_1}{b} \right) \quad (3)$$

which, subject to the conditions,

- (i)  $L_1 = L_2 = L_3$ ,
- (ii)  $L_1 + L_2 \ll a + b$ ,
- (iii)  $\frac{a}{b} = \frac{Q + R}{S - R}$ ,

reduces to

$$P = \frac{R}{S}Q \quad (4)$$

Lead resistances are, in general, less than  $1 \Omega$  and can be made equal within  $0.1\%$  using the bridge itself for this comparison. This is adequate to satisfy condition (i). Maximum allowable lead resistances to satisfy condition (ii)

were discussed by Gautier.<sup>(2)</sup> To check on condition (iii), the bridge is connected as shown in Fig. 1(b) and if it balances for all values of  $Q$  and  $a$ , (iii) is obviously satisfied. In practice, there will be a small out-of-balance current due to the fact that bridge resistors will invariably differ slightly from their nominal values. Hall<sup>(3)</sup> gave some numerical

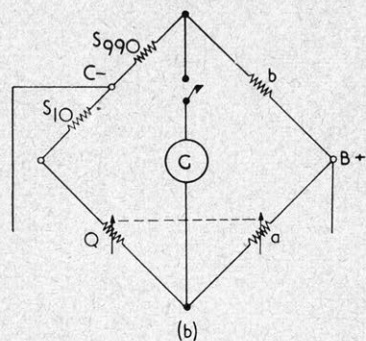
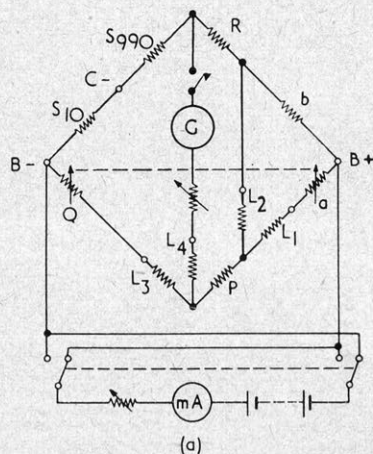


Fig. 1. The Smith bridge circuit

(a) Connexions for resistance measurements; and (b) connexions for the  $a/b$  ratio test.  $S = b = 1000 \Omega$ ,  $R = 10 \Omega$ ,  $a = (Q + 10)/0.99 \Omega$ ,  $L_1, L_2, L_3, L_4$  = thermometer leads.

data of the effect of such errors on calculated temperatures. For the present purpose, a more general treatment will be adopted. Equation (3) can be written in the form

$$P = \frac{R}{S}Q + \frac{R}{S}E \quad (3a)$$

and if  $L_1 = L_2 = L_3 = L$  (say), then

$$E = L + \frac{SbL}{R(a+b+2L)} \left( \frac{Q+L}{S} - \frac{a+L}{b} \right) \quad (5)$$

If (iii) were attained, the magnitude of  $E$  would depend only on that of  $L$  and normally would be less than  $150 \mu\Omega$ : an error which is sufficiently small to be neglected. In fact (iii) will not in general be attained as that  $E$  will depend on the values of its components  $Q$ ,  $a$ ,  $b$ ,  $S$  and  $R$ . The variation of  $E$  can be determined by partial differentiation of  $E$  with respect to these components:

$$\Delta E = \frac{L}{RA^2} \left\{ bA \cdot \Delta Q - [b(Q+L) + S(b+L)]\Delta a + \right. \\ \left. + [(a+2L)(Q+L) + S(a+L)]\Delta b - A(a+L)\Delta S - \right. \\ \left. - [b(Q+L) - S(a+L)] \frac{A}{R} \Delta R \right\} \quad (6)$$

where  $A = a + b + 2L$  and  $\Delta Q$ ,  $\Delta a$ , etc., are independently determined corrections. For a reasonably well adjusted bridge,  $\Delta E$  will be so small relative to  $Q$  (see Table 1 below),

Table 1. *Subsidiary ratio corrections*

$Q$ arm setting, $\Omega$	$\Delta Q$ , $\Omega$	$\Delta a$ , $\Omega$	$\frac{\Delta E}{L}$
500	0.040	0.025	0.001
$10 \times 100$	0.070	0.045	0.001
$1 \times 1000$	0.512	0.153	0.018
2000	0.862	0.210	0.022
2500	0.900	0.220	0.019
3000	1.195	0.200	0.025
3500	1.220	0.210	0.022
4000	1.475	0.150	0.026
5000	1.830	0.190	0.027
6000	2.180	0.230	0.028
6700	2.210	0.270	0.025
7000	2.580	0.255	0.029
8000	2.915	0.240	0.030

that its determination to the nearest 5% will, in general, be quite sufficient. Since  $L$  is very small relative to the other resistors it can be neglected in comparison with  $a$ ,  $b$  and  $Q$  in (6). Nominal values can be used for  $b$  (1000  $\Omega$ ),  $S$  (1000  $\Omega$ ) and  $R$  (10  $\Omega$ ), and the term involving  $\Delta R$  can be omitted since it is negligible compared to the other terms. Hence (6) becomes

$$\Delta E \approx \frac{100L}{a+1000} \left( \Delta Q - \frac{Q+1000}{a+1000} \Delta a \right) + \\ + \frac{aL}{10(a+1000)} \left( \frac{Q+1000}{a+1000} \Delta b - \Delta S \right)$$

which can, in turn, be reduced to

$$\Delta E \approx \frac{100L}{Q+1000} (\Delta Q - \Delta a) + \frac{QL}{10(Q+1000)} (\Delta b - \Delta S) \quad (7)$$

at least for temperature measurements above  $0^\circ \text{C}$  where  $a$  will differ from  $Q$  by less than 2%.

In the D.S.L. bridge  $\Delta b - \Delta S$  has been approximately  $0.1 \Omega$  for the last eight years, which means that for  $Q$  values corresponding to the temperature range  $0^\circ \text{C}$  to  $500^\circ \text{C}$  and for a lead resistance of  $0.5 \Omega$ , the contribution of the final term of (7) to  $\Delta E$  varies from about  $0.003$  to  $0.005 \Omega$ .

Since the resulting errors in temperature measurements are negligible, (7) can be finally simplified to

$$\Delta E \approx \frac{100L}{Q+1000} (\Delta Q - \Delta a) \quad (8)$$

$\Delta Q$  and  $\Delta E$  will be the only remaining sources of error which might affect calculated temperatures significantly. Hence, instead of (3) reducing to (4), it reduces to

$$P = \frac{R}{S} (Q + \Delta Q + \Delta E) \quad (9)$$

where  $\Delta E$  is defined by (8).

Values of  $\Delta E/L$  for the D.S.L. bridge are shown in Table 1. They have changed very little during the last four years, as might be expected, for the  $Q$  and  $a$  coils have similar drift rates. Values of  $\Delta a$  are determined from the out-of-balance current measured during the  $a/b$  ratio tests.<sup>(4)</sup> The measurement of  $\Delta Q$  has yet to be discussed. Even if lead resistances reach  $1 \Omega$ , the errors in temperature measurements caused by the values of  $\Delta E/L$  given in Table 1 are less than  $0.001^\circ \text{C}$  at any point within the platinum thermometer range, and less than  $0.0005^\circ \text{C}$  within the fundamental interval.

#### FURTHER SOURCES OF ERRORS IN RESISTANCE MEASUREMENTS

There are other sources of errors in resistance measurements, such as inadequate temperature control of the bridge coils and inadequate insulation resistance. They can be checked relatively easily and will not be discussed here.

Errors due to changes in the resistance of the contacts of the decade switches can become significant notwithstanding the  $1/100$  ratio arms. To avoid these errors, the switches must be kept scrupulously clean from sludge which is continuously formed around them by oil spray from the constant temperature bath mixing with small metal particles resulting from the movement of the brushes. If this sludge is allowed to accumulate on and between the contact surfaces, it can cause irregular variations exceeding  $0.01 \Omega$  in the sum of the contact resistances and can also lower the insulation resistance between the  $Q$  and  $a$  arms. For this reason, the switch contacts on the D.S.L. bridge are cleaned with toluol at monthly intervals. If the switches are clean, several rapid sweeps over all ten contacts will leave the bridge reading unaffected.

Short term fluctuations and drifts in the resistances of the bridge coils constitute the most serious obstacle to the realization of precision measurements. They are most noticeable in the  $1000 \Omega$  resistors but are also apparent in the  $100 \Omega$  coils. (It would be necessary to take special steps to detect fluctuations in coils lower than  $100 \Omega$  since they no longer exercise any significant effect on total bridge resistance.) Consequently, it is often impossible to make accurately reproducible readings even from day to day and, in the absence of means for either preventing or monitoring these resistance fluctuations, temperature measurements cannot generally be made to much better than  $\pm 0.002^\circ \text{C}$  even within the fundamental interval.

#### THE USE OF A DECADE OF STABLE $10 \Omega$ RESISTORS FOR SMITH BRIDGE CALIBRATION

The problem of bridge resistance fluctuations could be solved by redesigning the bridge<sup>(5)</sup> or by replacing the relevant bridge coils.<sup>(6)</sup> Either method, however, would be very



costly and could hardly be applied to an existing bridge. Instead, the D.S.L. bridge is simply and quickly calibrated when required, sometimes before every reading, by using it to measure a decade of stable 10  $\Omega$  manganin resistors.<sup>(7)</sup> Although such a procedure permits a check only on the 1000  $\Omega$  coils and the sum of the 100  $\Omega$  coils, these relatively few measurements will result in a satisfactory calibration, provided the following conditions are satisfied.

- (1) It must be possible to establish a sufficiently accurate relation between the correction for each 100  $\Omega$  dial setting and that for the entire 100  $\Omega$  decade.
- (2) Significant errors in the lower four of the six  $Q$  arm decades must be proportional to corresponding resistance readings or equal for all such readings.
- (3) Significant errors due to the  $a/b$  subsidiary ratio must satisfy the same requirements.

Condition (3) has been fully dealt with above. To establish (1) and (2), it is necessary to fully calibrate the bridge preferably more than once during the first few years of its life-time. Some results obtained during two full calibrations of the D.S.L. bridge are shown in Table 2(a). They are given for the three higher decades only. The resistors of the three lower decades, namely the 0.01  $\Omega$ , the 0.1  $\Omega$  and the 1  $\Omega$  decades, have at no stage deviated significantly from their respective nominal values. Concerning the higher decades, Table 2(a) shows that the small errors in the 10  $\Omega$  coils remained adequately stable and it should be safe to assume that this behaviour is still continuing. The resistances of the 100  $\Omega$  coils measured in 1951 were very nearly proportional to those measured in 1947. Table 2(b), which gives examples of results obtained with the new calibration method, indicates that this proportionality has been preserved. Since the total correction for this decade can be readily determined by a measurement against one of the 10  $\Omega$  calibrating resistors, corrections for each coil can be deduced from the results of earlier calibrations, or, more simply, by assuming that every coil of the decade has the same correction, namely one-tenth of the measured decade correction. Table 2(a) shows that correct values would still be obtained for some of the dial settings, and that the error for any other setting would not exceed 0.0005° C.

Since the  $R/S$  ratio will never be exactly 1/100 and since the  $a/b$  subsidiary ratio also has a slight effect on results, corrections obtained by this method differ from those which would be obtained by a direct potentiometric calibration of the  $Q$  arm. However, any changes in the  $R/S$  ratio affect all bridge readings by exactly equal proportions, while, at least in the case of the D.S.L. bridge, the  $\Delta E$  term of (9) and other error terms that have been mentioned are either small enough to be virtually proportional to these readings or are virtually constant. Hence, provided thermometers are used for which  $L$  is less than 0.5  $\Omega$  and provided reasonable care is taken when this new calibration method is used, the sum of the various errors originating in the bridge will not cause errors in temperature measurement exceeding those given in the summary, which are, in the large majority of cases, small enough to be neglected in comparison with other errors to which temperature measurements are subject.<sup>(8)</sup>

#### ACKNOWLEDGEMENTS

Acknowledgement is made to the Chief Scientist, Department of Supply, Australia, for permission to publish this

Table 2. D.S.L. Smith bridge:  $Q$  arm calibrations

#### (a) Potentiometric method

Relative accuracy  $\pm 1$  p.p.m. or  $\pm 0.001 \Omega$

Dial marking	Sections	Resistance at 30° C (in absolute ohms)	
		1947	1951
X by 1000	1	1 000.627	1 000.540
	2	2 001.09	2 000.90
	3	3 001.52	3 001.23
	4	4 001.94	4 001.52
	5	5 002.43	5 001.90
	6	6 002.91	6 002.28
	7	7 003.34	7 002.66
	8	8 003.91	8 003.04
	9	9 004.31	9 003.41
	10	10 004.78	10 003.78
X by 100	1	100.008	100.007
	2	200.027	200.021
	3	300.037	300.028
	4	400.060	400.043
	5	500.081	500.061
	6	600.104	600.079
	7	700.124	700.092
	8	800.135	800.099
	9	900.150	900.109
	10	1 000.162	1 000.118
X by 10	1	10.001	10.001
	2	20.002	20.002
	3	30.003	30.003
	4	40.004	40.004
	5	50.005	50.005
	6	60.005	60.006
	7	70.006	70.007
	8	80.008	80.008
	9	90.009	90.009
	10	100.010	100.010

#### (b) New method

Relative accuracy  $\pm 1$  p.p.m.

Dial marking	Sections	Resistance at 30° C		
		January 1955	April 1955	July 1955
X by 1000	1	1 000.504	1 000.516	1 000.524
	2	2 000.843	2 000.869	2 000.885
	3	3 001.174	3 001.202	3 001.224
	4	4 001.443	4 001.486	4 001.517
	5	5 001.786	5 001.841	5 001.882
	6	6 002.124	6 002.190	6 002.242
	7	7 002.52	7 002.60	7 002.65
	8	8 002.84	8 002.93	8 002.99
	9	9 003.14	9 003.24	9 003.31
	10	10 003.44	10 003.55	10 003.64
X by 100	10	1 000.064	1 000.077	1 000.084

paper. The author also wishes to thank Mr. R. G. Ackland for many helpful suggestions during its preparation.

## REFERENCES

- (1) SMITH, F. E. *Phil. Mag.*, **24**, p. 561 (1912).
- (2) GAUTIER, M. *J. Sci. Instrum.*, **30**, p. 381 (1953).
- (3) HALL, J. A. *Phil. Trans. A*, **229**, p. 1 (1929-30).
- (4) GOODWIN, W. N. *Weston Engineering Notes*, **2**, No. 5 (1947).
- (5) BARBER, C. R., GRIDLEY, A., and HALL, J. A. *J. Sci. Instrum.*, **32**, p. 213 (1955).
- (6) BARBER, C. R., GRIDLEY, A., and HALL, J. A. *J. Sci. Instrum.*, **29**, p. 65 (1952).
- (7) LOWENTHAL, G. C., and ACKLAND, R. G. *J. Sci. Instrum.* To be published.
- (8) National Physical Laboratory. Notes on Applied Science, No. 12, "Calibration of Temperature Measuring Instruments," p. 4 (London: H.M.S.O., 1955).

## The damping effect of surrounding gases on a cylinder in longitudinal oscillation

By M. T. BROWNE, B.Sc., A.R.C.S., and J. R. PATTISON, B.Sc., Ph.D., A.Inst.P.,\* Department of Physics, Imperial College of Science and Technology, London

[Paper received 17 May, 1957]

The external damping influences on a longitudinally vibrating cylindrical bar are examined quantitatively. Experiments undertaken to confirm the theoretical estimations indicate a possible precision method for the determination of gas viscosities.

In a number of methods used for investigating internal damping in solids, the specimen is in the form of a cylindrical bar supported at a node of vibration so that it is able to vibrate under free-free conditions. Under such conditions, external sources of damping are present in addition to that under study. These are (a) viscous damping along the cylindrical surface; (b) acoustic radiation from the vibrating surfaces; and (c) damping loss in the specimen support. A theoretical evaluation of these damping sources may be made without difficulty.

### THEORETICAL TREATMENT OF EXTERNAL DAMPING

Consider a cylindrical bar of length  $2l$  and diameter  $2r$  with plane ends, supported at its centre. If the bar is set into free-free longitudinal oscillations about a central node, and the peak velocity along the axis of a thin disk section distant  $x$  from the node is  $u$ , then

$$u = U \sin(\pi x/2l) \quad (1)$$

If  $v$  denotes the peak radial velocity of the circumference of the disk element, then

$$v = V \cos(\pi x/2l)$$

But if  $\mu$  is Poisson's ratio for the bar material,  $V$ , the peak radial velocity at the node of longitudinal vibrations, is related to  $U$ , the peak axial velocity at the free ends of the bar, by

$$V = (\mu r/l)U$$

$$\text{Hence } v = (\mu r/l)U \cos(\pi x/2l) \quad (2)$$

A simple unit of damping is the damping capacity  $\Delta W/W$  used by Föppl,<sup>(1)</sup> where  $\Delta W$  is the energy absorbed in each cycle of vibration and  $W$  is the total energy of vibration. The

logarithmic decrement  $\delta$  is more commonly used and has the following relation to the damping capacity

$$\Delta W/W = 1 - e^{-2\delta}$$

so that  $\delta \simeq \Delta W/2W$  for small  $\delta$ .

For the bar under consideration, if  $\rho_M$  is the density of the material

$$W = \frac{1}{2} \rho_M \int_{-l}^l \pi r^2 u^2 dx$$

using equation (1)

$$W = \frac{1}{2} \pi r^2 l \rho_M U^2 \quad (3)$$

For the viscous damping along the cylindrical sides of the bar, the equation obtained by Stokes<sup>(2)</sup> may be used. The tangential force  $F$  on a unit plane area, moving at a velocity  $u \cos 2\pi ft$ , which varies sinusoidally with time  $t$  at a frequency  $f$ , owing to a medium of density  $\rho$  and viscosity  $\eta$  is given by,

$$F = u \cos 2\pi ft \cdot \sqrt{(\pi f \rho \eta)}$$

If we consider the surface area of a thin disk element of the bar  $\Delta x$  thick, the work done by the force  $F$  in time  $\Delta t$  is

$$F \cdot 2\pi r \cdot u \cos 2\pi ft \cdot \Delta t \cdot \Delta x$$

Hence  $\Delta W_V$ , the energy dissipated by the bar in overcoming viscous forces in each cycle of oscillation, can be obtained by summation over one cycle and over the length of the bar using equation (1) to substitute for  $u$ .

$$\Delta W_V = (\pi r l U^2 / f) \sqrt{(\pi f \rho \eta)}$$

From equation (3),  $\delta_V$  the decrement corresponding to viscous damping is

$$\delta_V = \Delta W_V / 2W = (1/f r \rho_M) \sqrt{(\pi f \rho \eta)} \quad (4)$$

The calculation of the damping effects due to the acoustic radiation from a vibrating bar is simplified by considering

\* Now at British Iron and Steel Research Association, London.