THE THERMAL CONDUCTIVITY OF STEAM AT ATMOSPHERIC PRESSURE

by

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PREFACE

In this thesis work carried out by the author to measure the thermal conductivity of steam at atmospheric pressure in the temperature range 100°C - 700°C is reported. This work was undertaken in view of the discrepancies which exist in the experimental data at atmospheric pressure. In particular, the serious differences which exist at the high temperatures, between the results of Russian experimenters, who give higher values than those given by American and German workers, needed investigation.

A complete test rig, designed and developed by the author, which may be used for accurate thermal conductivity measurements on gases at atmospheric pressure in the temperature range 100°C - 700°C, is described. An absolute steady state method, utilising two concentric cylinder type cells, one made of brass, used for preliminary measurements in the range 140°C - 160°C and the other of silver, was used. The thermal conductivity of steam in the temperature range 100°C - 700°C, at atmospheric pressure, has been measured with a probable accuracy estimated to be within ± 1.5% - ± 2%.

The results obtained confirm Russian observations at the higher temperatures and it is hoped that these results will help to resolve finally the inconsistencies in the experimental data. A fresh assessment of all the experimental data is given by the author where arguments in favour of both the lower and the higher atmospheric line are discussed. A new correlation of experimental data has been undertaken and a reduction in the tolerances put on the eqbation defining the atmospheric line from $\pm$ 3% in the range 100°C - 400°C and $\pm$ 4% in the range 400°C - 700°C to $\pm$ 2% over the complete range 100°C - 700°C is now recommended.

Included in the appendices are descriptions of two additional pieces of work carried out by the author. The first describes the experimental measurement of the thermal conductivity of argon and nitrogen in the range 100°C - 300°C at atmospheric pressure utilising both the silver and brass cells. The results obtained show good agreement with recent published values. The mean deviation of the points from the recently published correlations, for these gases, of Vargaftik and Zimina is some 1%. In the second a new test rig, designed by the author for thermal conductivity measurements on both gases and liquids at atmospheric pressure and moderate temperatures, is described. The method of measurement used was the same as that used for the steam measurements but a completely new cell utilising an emitter constructed of an anisotropic material, pyrolytic graphite, was used. As a result of using this material a short yet thick cell was constructed and hence certain problems of cell and thermostat design and construction were reduced. The preliminary results obtained are estimated to be accurate to within $\pm$ 2%.

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CHAPTER I

SURVEY OF PREVIOUS EXPERIMENTAL WORK

I(1) Introduction

It is the purpose of this chapter to review the existing situation concerning the experimental measurement of the thermal conductivity of steam at atmospheric pressure.

Since in this work the author is concerned with the variation of the coefficient of thermal conductivity of steam with temperature at atmospheric pressure the following summary of previous experiments takes into account only measurements which have been made at or near atmospheric pressure. The most recent survey of experiments of thermal conductivity of water and of steam at high pressures has been given by Venart (1) in 1964.

Over the years many users of different tables of thermal conductivity values have accepted these values without realising that the primary data on which the tables were based were subject to large errors. On surveying the discrepancies which exist in experimental data at atmospheric pressure the particularly serious differences which exist at higher temperatures become apparent.

I(2) Summary of Previous Experiments

In nearly all previous investigations a steady state method utilising cells of cylindrical geometry, namely hot wire cells and concentric cylinder cells, has been employed. Methods of measurement are described in Chapter II.

Among the earliest data cited in references concerning the thermal conductivity of steam is the work of Moser (2). In his work, published in Germany in 1913, he measured the thermal conductivity of some 25 gases and vapours. The hot wire method, first successfully used by Schleiermacher (3), was employed. Moser obtained two values for the thermal conductivity of steam at 46°C and 100°C. The values were obtained relative to air conductivity measurement and the pressures at which measurements were made were, of course, below atmospheric. Moser did not consider that the data for these two points were very accurate because of the low pressures at which the measurements were made. It should also be noted that the value for the thermal conductivity of air which he used was low. Even when corrected by using the now accepted value for the thermal conductivity of air his values still are some 4% lower than those of other workers.

Some 21 years later the work of Milverton (4), who was interested in finding the effect of pressure on the thermal conductivity of water vapour, was published in Britain. The hot wire method of measurement was used. The diameter of the wire was 0.1 mm and the internal diameter of the tube was 8 mm. The thermostat which he used was a water bath which could not be operated at temperatures above 100°C and the pressures at which measurements were made varied from 4 to 36 cmHg. Milverton did not take into account the effects of temperature discontinuities at the wire surfaces. Hence it is thought he gained an exaggerated impression of the influenne of pressure on the thermal conductivity values obtained.

The first attempt to measure the thermal conductivity of steam over reasonably large ranges of temperature and pressure was undertaken by Vargaftik (5) in 1937. Some 21 measurements were performed for steam at near atmospheric pressure in the range 70°C-480°C. Results are also given for steam at pressures ranging from 5 to 30 atmospheres in the temperature range 250°C to 350°C. The method of measurement used was again the hot wire method. The wire, made of platinum, was 0.1080 mm diameter and the receiver was a thin glass tube some 0.8 mm internal diameter. In order to establish the absence of convection in the test cell a series of tests were carried out on nitrogen at temperatures of approximately 40°C and 60°C and at pressures of 1 to 90 atmospheres. From these tests it was shown that the value of thermal conductivity obtained did not vary for different temperature differences between the wire and receiver indicating that convective heat transfer across the steam gap was negligible. These tests also served to give the thermal conductivity of nitrogen in this range. The steam values obtained in this work differ greatly from the theoretical values suggested at that time by Jacob (6) who used Moser's data. Vargaftik's values are approximately 10% higher.

This first Russian work was followed in 1946 by the experiments of Vargaftik and Oleshchuk (7) who published 7 measurements over a much wider range of temperature, 50°C - 900°C. For work at moderate temperatures the receiver tubes were made of glass but these had to be replaced by quartz tubes for high temperature work.

Much attention was paid by these workers to the effects of temperature discontinuity at the wire surface which is of particular significance at high temperatures. In addition to this work Vargaftik(8) in 1948 published some 12 new values in the same temperature range. These results, however, showed higher values than those obtained in earlier work (see figure I(3)).

In 1950 the work of American experimenters Keyes and Sandell (9) was published. Keyes and Sandell obtained results for steam in the temperature range 100°C - 350°C and at pressures ranging from 0.03 to 150 atmospheres. The cell which they used was a silver concentric cylinder cell with guard heating supplied at one end only. The cell was calibrated using nitrogen as the calibrating gas. The inner cylinder of the cell had a diameter of 0.8512" and the receiver was 0.9012" internal diameter. Using the experimental values which they obtained they set up an empirical equation for the thermal conductivity of steam from which values were given to 500°C. This data showed severe disagreement with all of the Russian work, being lower than Russian values by some 30% at 500°C. Keyes and Vines(10) have, however, in a recent work explained that this earlier work of Keyes and Sandell was in error due to the fact that their knowledge of the thermal conductivity of nitrogen at that time proved insufficient and that a higher value for the thermal conductivity of nitrogen should have been used. On correcting the results the values of Keyes and Sandell are in tolerable agreement with Russian values.

In view of this new data presented by Keyes and Sandell, Vargaftik and Smirnova (11) made another series of measurements in the range $240^\circ C$ - $500^\circ C$ at near atmospheric pressure in order to check the accuracy of the earlier Russian data. In this work they performed two series of tests. The first set of results, some 5 points, was obtained using a hot wire apparatus. The second set, some 4 points, was obtained by using a silver concentric cylinder cell with guard heating supplied at both ends. The diameter of the silver emitter was 25.346 mm and the internal diameter of the receiver was 27.250 mm. The results of these experiments showed agreement with earlier Russian data. The authors pointed out in this work that the value for the thermal conductivity of nitrogen used by Keyes and Sandell in calibrating their cell was low. Using Russian data for the thermal conductivity of nitrogen they recalculated the results and showed them to be in agreement with their values.

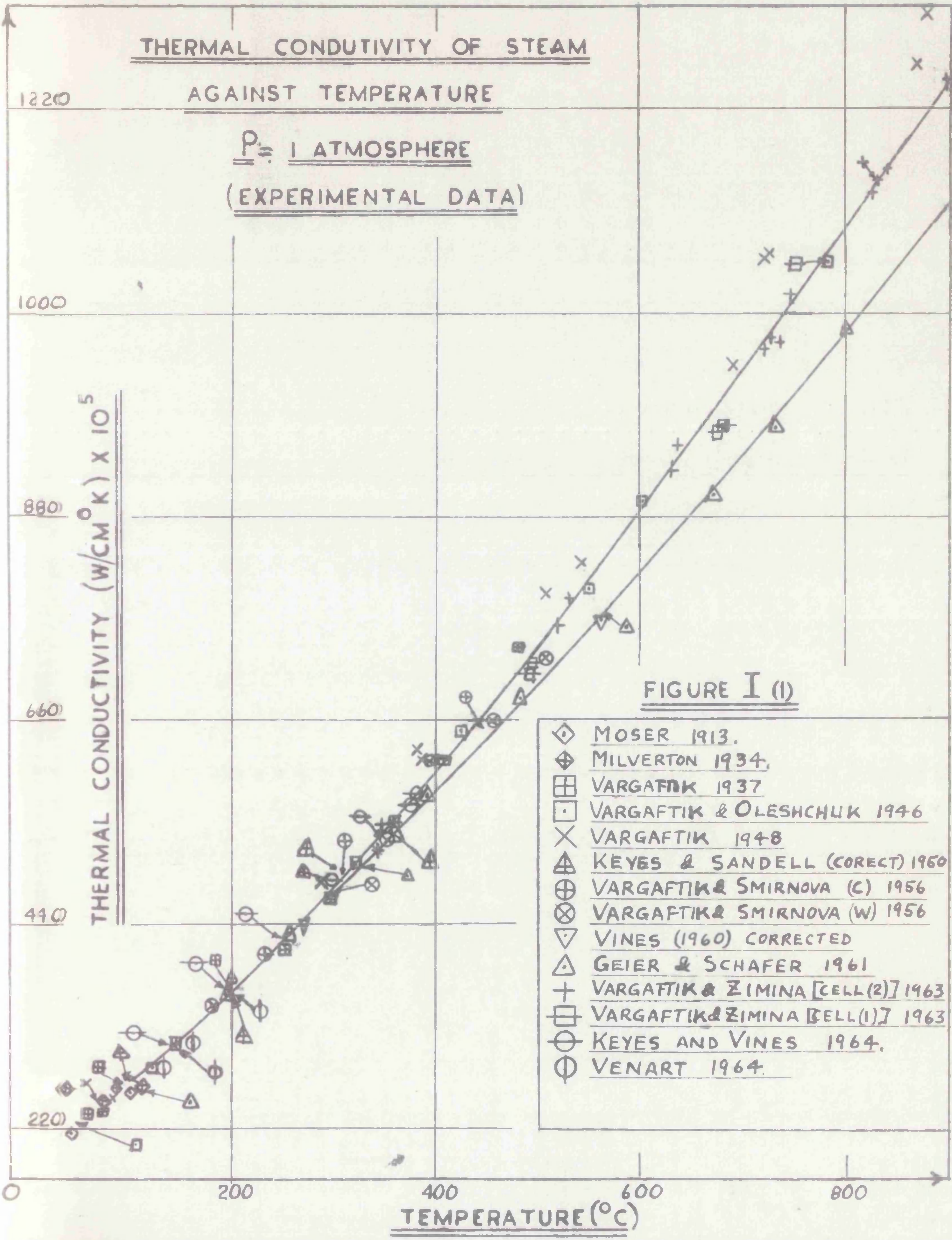
Some 4 years after these experiments of Vargaftik and Smirnova the work of Australian experimenter Vines (12) was published in America. He made measurements on air, argon, nitrogen, carbon dioxide and CO_2/N_2 mixtures in the temperature range 240 - $900^\circ C$ at atmospheric pressure. He also reported two measurements for steam at $270^\circ C$ and $560^\circ C$. Since the external portions of this apparatus were not heated the steam measurements were made at a pressure of some 0.2 cm Hg. The cell which he used was of the concentric cylinder type with guard heating supplied at each end. The diameter of the platinum inner cylinder was 6 mm and the internal diameter of the platinum receiver was 10 mm. The cell constant was calibrated so that the experimental values obtained for air, argon, carbon dioxide and nitrogen at approximately $250^\circ C$ were in agreement with accepted values. The value for steam obtained by Vines at 270°C was in agreement with Russian data but the 560°C value was some 5% lower. Vines did not make corrections for temperature discontinuities at the cell surfaces. It should also be noted that, due to the cell dimensions which he chose (i.e. a gap size of some 2 mm) and also to the reasonably high emissivity of platinum, the correction which he had to apply for radiant heat transfer was very large. At temperatures above 750°C the radiant heat transferred accounted for approximately half the heat dissipated in the emitter.

A year after the work of Vines was completed the results of the experiments of two German workers Geier and Schafer (13) were published. They obtained values for H_2, CO_2, CO, O_2, Air, N_2, CH_4, C_2H_6, NH_3 and also some 13 values for steam at near atmospheric pressure in a temperature range extending up to 1200°C. A hot wire cell was used. For steam measurements the wire was made of platinum 0.1 mm diameter and the receiver was a quartz tube. The cell constant was determined by calibrating with argon. At lower temperatures the steam values which they obtained are in reasonable agreement with Russian data. At higher temperatures, however, their values suggest a much lower atmospheric line. The divergence from Russian data increases as temperature increases, being some 9% at 700°C, from the most recent Russian values. Their steam measurements were made at a pressure of some 150 mmHg but no correction appears to have been made by the authors for 'thermal jump'. It seems unlikely, however, that application of this correction would be enough to increase their values to agree with Russian data. Although for this reason their data at high temperatures must be considered as being somewhat low.

In order, again, to check earlier work Russian experimenters Vargaftik and Zimina (14) in 1963 undertook experiments to remeasure the atmospheric line for steam. Utilising two hot wire cells in two separate series of experiments they obtained some 21 points at atmospheric pressure in the temperature range 300°C - 900°C. The dimensions of cell (1) were platinum wire diameter 0.157 mm and internal diameter of quartz tube 4.07 mm and for cell (2) the platinum wire diameter was 0.142 mm and internal diameter of the quartz tube 2.95 mm. Details of experiments carried out at the higher temperatures to determine the effects of temperature discontinuities at the wire surfaces are given. They use the experimental points obtained in this work to derive an equation defining the atmospheric line in the temperature region 100°C - 900°C. This equation was accepted by the Thermal Conductivity Panel of the Sixth International Conference on the Properties of Steam in Paris in 1964, as defining the atmospheric line in the temperature range 100°C - 700°C within certain agreed tolerances. The experimental values obtained and the values given by this equation give lower values than those given by Vargaftik (8) in 1948 (see figure (2)) but they are still substantially higher than the values quoted by the German experimenters Geier and Schafer (13) and those suggested by Vines (12) and Keyes and Vines (10).

In 1964 Keyes and Vines (10) published their work on steam which had been performed several years earlier. They made measurements in the temperature range 139°C - 380°C at pressures up to 200 atmospheres. While three of the points given were obtained at pressures only slightly above 1 atmosphere, the 6 points which may be obtained from this work are calculated by extrapolation of their high pressure data. It should also be noted that the experimental points of Keyes and Sandell (9), for the temperatures at which they made measurements, are also obtained by extrapolation of pressure data. These extrapolated points are included because the work of Keyes, since he has indicated his preference for a lower atmospheric line, is of particular significance when assessing the experimental data. In this recent work of Keyes and Vines (10) a silver concentric cylinder cell with guard heating supplied at one end was again used. The diameter of the inner cylinder was 0.900225" and the internal diameter of the receiver was some 0.94". Utilising this work and the work of others they advance correlating equations and offer criticism of Russian high temperature data. This is more fully discussed in the next section of this chapter. They also state that, due to an error in calibrating the cell constant in the work of Vines (12), the steam values quoted in this paper should be reduced by 2½%. This increases the divergence of Vines 560°C point with Russian data to some 7.2%.

The most recent experiments to measure steam at atmospheric pressure have been carried out by Venart(1). In his work he measured the thermal conductivity of water and of steam at temperatures between 17°C and 250°C and at pressures from 1 to 300 atmospheres. He used a concentric cylinder apparatus with guard heating



THERMAL CONDUTIVITY OF STEAM AGAINST TEMPERATURE
P = 1 ATMOSPHERE
(EXPERIMENTAL DATA)
FIGURE I (1)
MOSER 1913.
MILVERTON 1934.
VARGAFTIK 1937
VARGAFTIK & OLESHCHUK 1946
VARGAFTIK 1948
KEYES & SANDELL (CORECT) 1960
VARGAFTIK & SMIRNOVA (C) 1956
VARGAFTIK & SMIRNOVA (W) 1956
VINES (1960) CORRECTED
GEIER & SCHAFER 1961
VARGAFTIK & ZIMINA [CELL(2)] 1963
VARGAFTIK & ZIMINA [CELL(1)] 1963
KEYES AND VINES 1964.
VENART 1964
THERMAL CONDUCTIVITY (W/CM °K) X 10^5
1220
1000
880
660
440
220
0
200
400
600
800
TEMPERATURE (°C)

supplied at both ends. The cell was made of a copper chromium alloy, 'Hidurel 6'. The diameter of the emitter was some 2.9656 cm and the gap between emitter and reciever was nominally 5×10^{-2} cm. In his work he was interested mainly in measuring the thermal conductivity of water and of steam at high pressures. He did, however, publish some points for steam at atmospheric pressure in the temperature range 130°C to 200°C. The values which he obtained are within the tolerances agreed by the Sixth International Conference on the Properties of Steam.

I(3) Discussion of Experimental Data:- The Need for Remeasurement of the Atmospheric Line

A plot of all the experimental data is shown in figure I(1). From this the serious differences between the Russian data and the values reported by Geier and Schafer and Vines are immediately apparent.

From the opinions expressed in the papers it would appear that a higher atmospheric line is favoured by Vargaftik and associates and that a lower line is favoured by Keyes and Vines, Keyes and Sandell, Vines and Geier and Schafer.

If the works apparently in favour of a lower line are first considered it will be noted that since his earliest measurements on steam Keyes has always predicted lower values than those favoured by Russian workers. Many tabulations such as those of Lenoir (15), Keenan and Keyes (16) and Keyes (17) have been based on Keyes data. In the recent work by Keyes and Vines (10) the equation which they used to define λ_0 (the coefficient of thermal conductivity at zero pressure) between 100°C and 700°C was

$$\lambda_o = \frac{0.01842 T^{\frac{1}{2}}}{1 + \frac{5485\tau}{10^{12\tau}}} \qquad \ldots\ldots \text{ I (A)}$$

(Note: This type of equation has been successfully used by Keyes to correlate λ_o for several gases).

(where units of λ_o are $^W/m\ ^oK.$; T is the temperature (^oK) and τ is $\frac{1}{T}$).

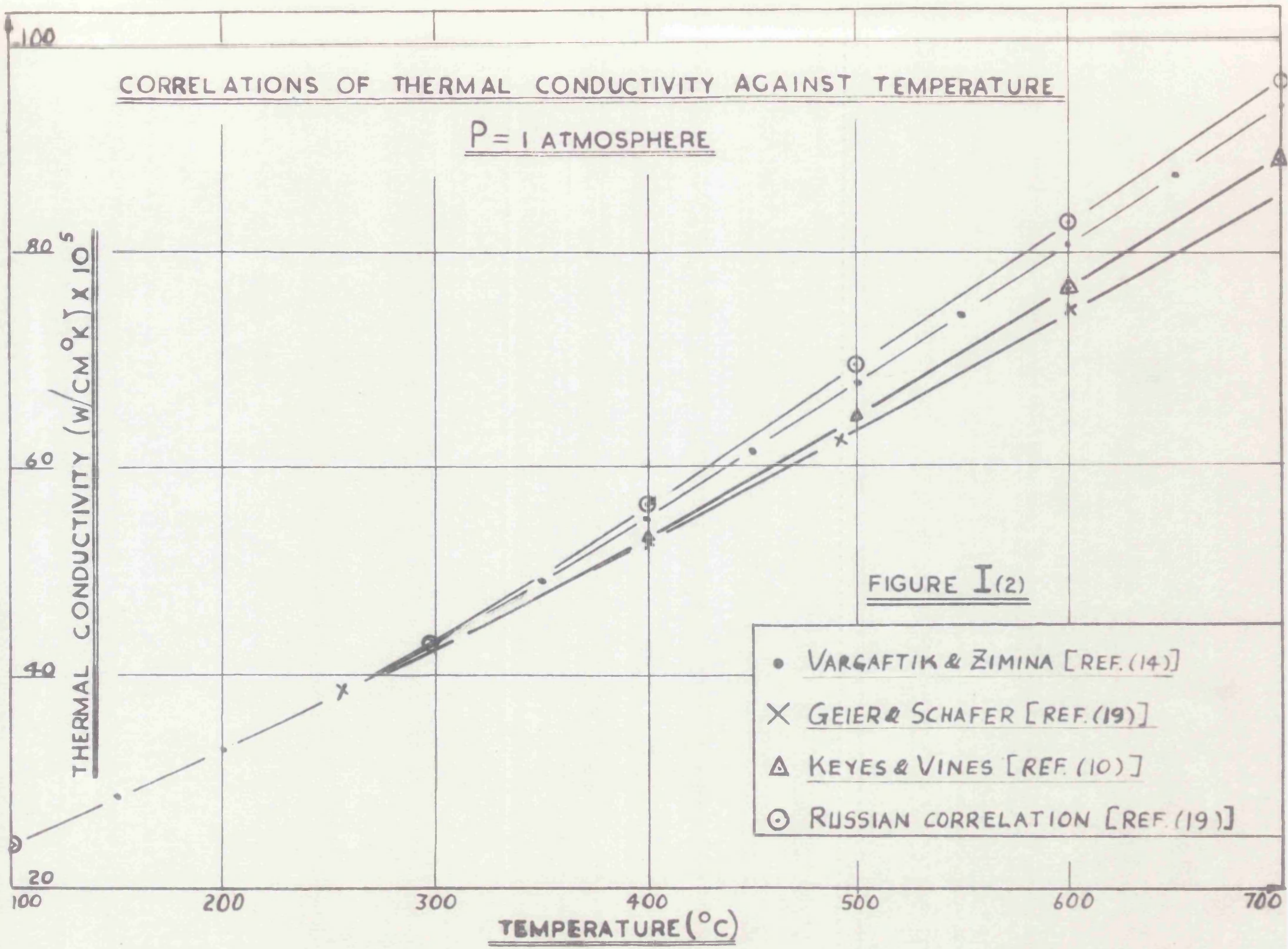
The works which they used to obtain this equation were those of Vines (12) and Keyes and Vines (10). They did not use the work of Geier and Schafer in their correlations although this work supports their claim for a lower line. Here it is perhaps worthwhile noting that both of the high temperature works (Vines (12) and Geier and Schafer (13)) performed outside Russia suggest lower values.

Keyes and Vines state that they consider that the Russian high temperature values are excessively high. They substantiate this claim by using two equations to correlate the works of Vargaftik and associates. The first equation for points below 400°C is

$$\lambda_1 = \frac{0.0155 T^{\frac{1}{2}}}{1 + \frac{4600\tau}{10^{12\tau}}} \qquad \ldots\ldots \text{ I(B)}$$

(where λ_1 is the coefficient of thermal conductivity of steam at atmospheric pressure).

The second equation for points above 400°C is



CORRELATIONS OF THERMAL CONDUCTIVITY AGAINST TEMPERATURE
P = 1 ATMOSPHERE
THERMAL CONDUCTIVITY (W/CM °K) X 10^5
100
80
60
40
20
100
200
300
400
500
600
700
TEMPERATURE (°C)
VARGAFTIK & ZIMINA [REF. (14)]
GEIER & SCHAFER [REF. (19)]
KEYES & VINES [REF. (10)]
RUSSIAN CORRELATION [REF. (19)]

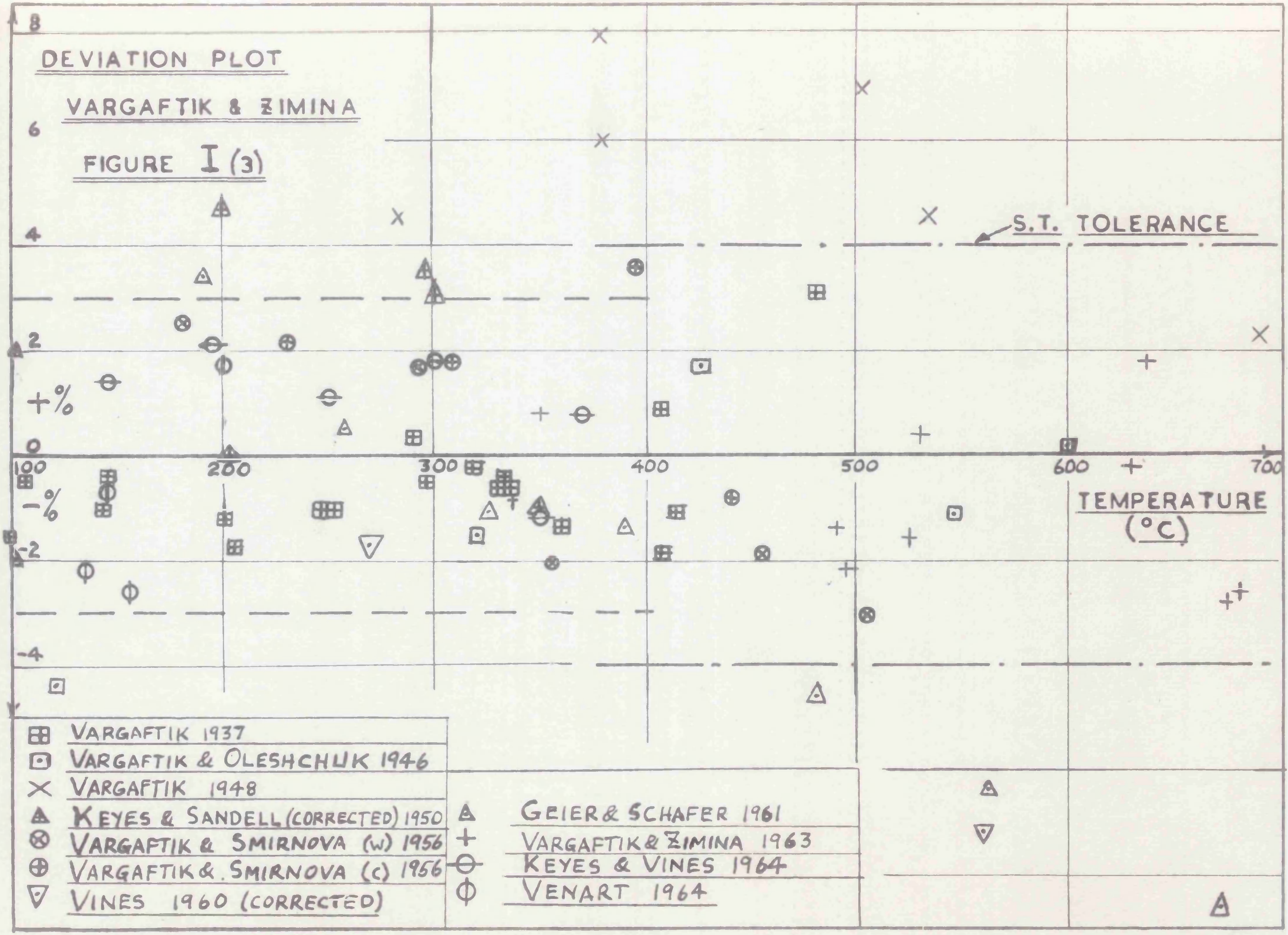
FIGURE I(2)

$$\lambda_1 = \frac{0.02122T^{\frac{1}{2}}}{-1 + \frac{7676\tau}{10^{12\tau}}} \qquad \ldots\ldots \text{ I (C)}$$

The first equation I (B) agrees fairly well with their own work. On plotting $\frac{T^{\frac{1}{2}}}{\lambda_1 \times 10^6}$ against $\frac{\tau \times 10^3}{10^{12\tau}}$ for equation I (C) they show that the intersection of the line obtained with the x-axis to the right of the zero point of the axis system requires that $\lambda_1 =$ ∞ at this point. This, they suggest, shows that Russian values at the higher temperatures are excessively large.

Also supporting the claim for a lower line is a most recent correlation carried out for the United States National Bureau of Standards (18). The table values quoted cover the range 250°K to 900°K. The tolerance which they put on the values between 710°K (436.85°C) and 900°K (626.85°C) is ± 5% and it should be noted that Vargaftik and Zimina's high temperature values do not lie within this tolerance.

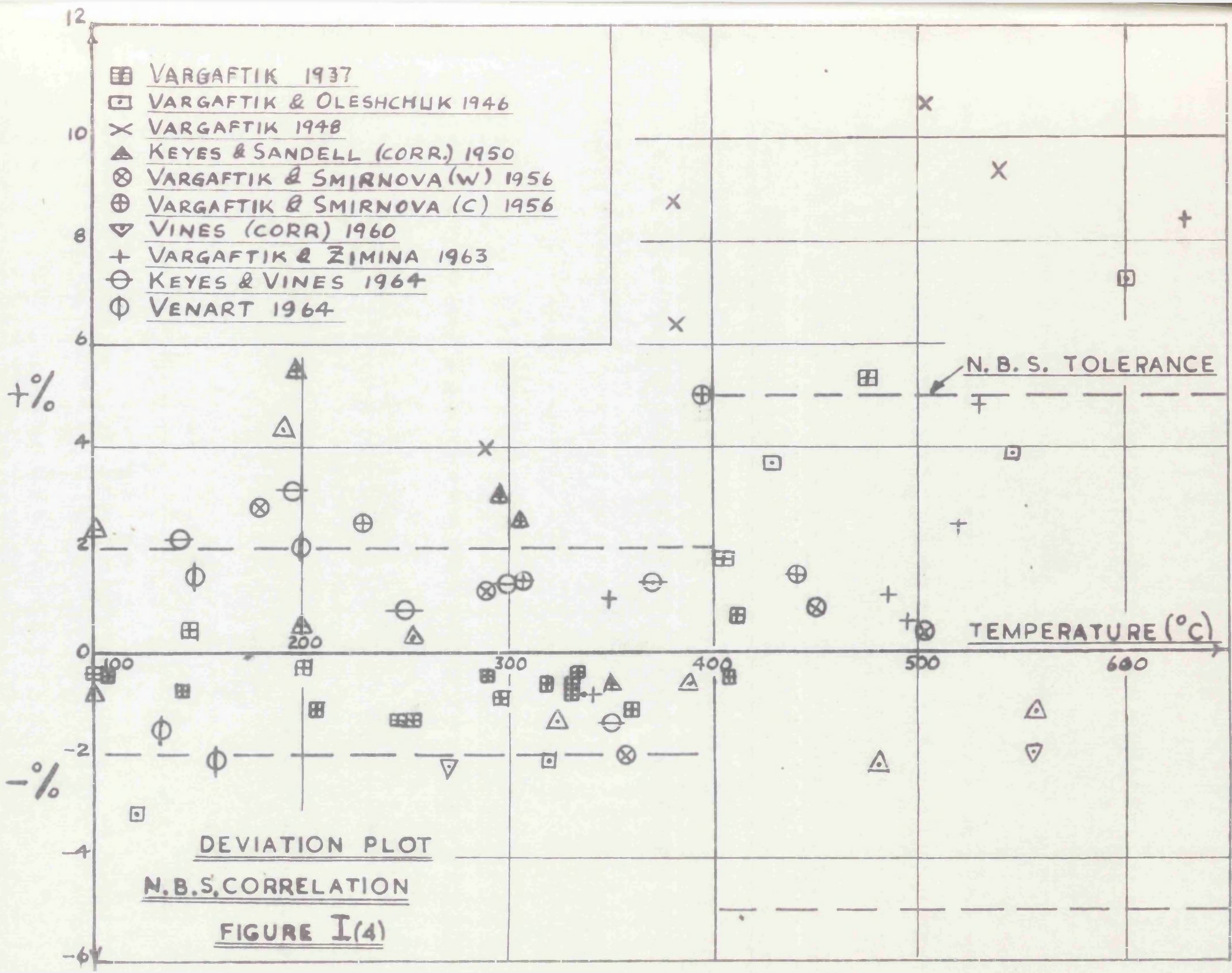
It is true, however, in the opinion of the author, that any correlation of experimental data must favour the higher Russian line. They have performed many more experiments . Indeed the Keyes and Vines equation I (A) which covers the temperature range 100°C - 700°C was correlated using only one experimental determination, the point of Vines at 560°C, between 400°C and 700°C. The correlating equation I (C) was formed using only Russian data presented by Vargaftik (26) in 1958. It did not include the latest experimental data of Vargaftik and Zimina whose correlation gives a slightly lower line at higher temperatures than that suggested in 1958, being


DEVIATION PLOT
VARGAFTIK & ZIMINA
FIGURE I (3)
8
6
4
2
0
-2
-4
+%
−%
100
200
300
400
500
600
700
TEMPERATURE (°C)
S.T. TOLERANCE
VARGAFTIK 1937
VARGAFTIK & OLESHCHUK 1946
VARGAFTIK 1948
KEYES & SANDELL (CORRECTED) 1950
VARGAFTIK & SMIRNOVA (W) 1956
VARGAFTIK & SMIRNOVA (C) 1956
VINES 1960 (CORRECTED)
GEIER & SCHAFER 1961
VARGAFTIK & ZIMINA 1963
KEYES & VINES 1964
VENART 1964

lower by 1.7% at 500°C, 2.9% at 600°C and 3.5% at 700°C. In addition Vargaftik has stated that the four points (see figure I (1)) obtained between 700°C and 900°C in his 1948 values are in error and should not be included in any correlation of data. Figure I (2) shows the atmospheric line of Vargaftik and Zimina and the line of Keyes and Vines. Also shown is a correlation of Russian data up to 1963 and a correlation of Geier and Schafer data presented by Bruges (19) in a report published in 1963.

A check on the validity of the Russian atmospheric line may be carried out by extrapolating their high pressure data back to atmospheric pressure. A plot of Russian values of thermal conductivity at pressures is plotted against ρ (where ρ is density) in figure I (5). From this it can be seen that the Russian data extrapolates well onto their atmospheric line. The values of Geier and Schafer are also shown on this plot and it can be seen clearly, that if a lower atmospheric line is correct then all of the Russian high pressure data will have to be re-examined. If as a guide to the accuracy of the works of Vargaftik and Zimina examination of the experimental work performed by these workers for Argon (20) and Nitrogen (21) is undertaken it will be seen that their values show good agreement with those of other experimenters.

From figure I (3) where the percentage deviations of all the experimental points from the equation of Vargaftik and Zimina against temperature are drawn it will be noted that the experimental points of Keyes and Sandell (corrected) and Keyes and Vines are in



DEVIATION PLOT

N.B.S. CORRELATION

FIGURE I(4)

tolerable agreement with this equation. Thus the only experimental works decidedly in favour of a lower line are the works of Geier and Schafer supported by the work of Vines.

When the Thermal Conductivity Panel of the Sixth International Conference on the Properties of Steam met in Paris in June 1964 several correlations of atmospheric data were considered. This meeting is reported by Bruges (22) who acted as co-ordinator. The proposals of the British, Russian and German delegations showed agreement but the proposal of the American delegation suggested again a somewhat lower atmospheric line. It was decided at this meeting to adopt the equation of Vargaftik and Zimina.

$$\lambda_1 . 10^4 = 176 + 0.587t + 1.04 \times 10^{-3} t^2 - 4.51 \times 10^{-7} t^3 \quad \ldots \text{I (D)}$$

(where λ_1 ($^W/m$ ^oK) is the thermal conductivity at atmospheric pressure and t (^oC) is the temperature).

This equation may be used to obtain the Skeleton Table Values between 100°C and 700°C and the tolerances put on this equation are

$$100 \leqslant t(^oC) \leqslant 400 : \pm 3\%$$

$$400 < t(^oC) \leqslant 700 ; \pm 4\%$$

In accepting this equation and these tolerances the reported high temperature values of Vines and Geier and Schafer as well as the work of Vargaftik performed in 1948 must be disregarded.

It appears most unsatisfactory that in the experimental data used to correlate equation I(D) the only actual experiments which have been performed at or near atmospheric pressure above the temperature of 250°C have been undertaken by the single Russian source

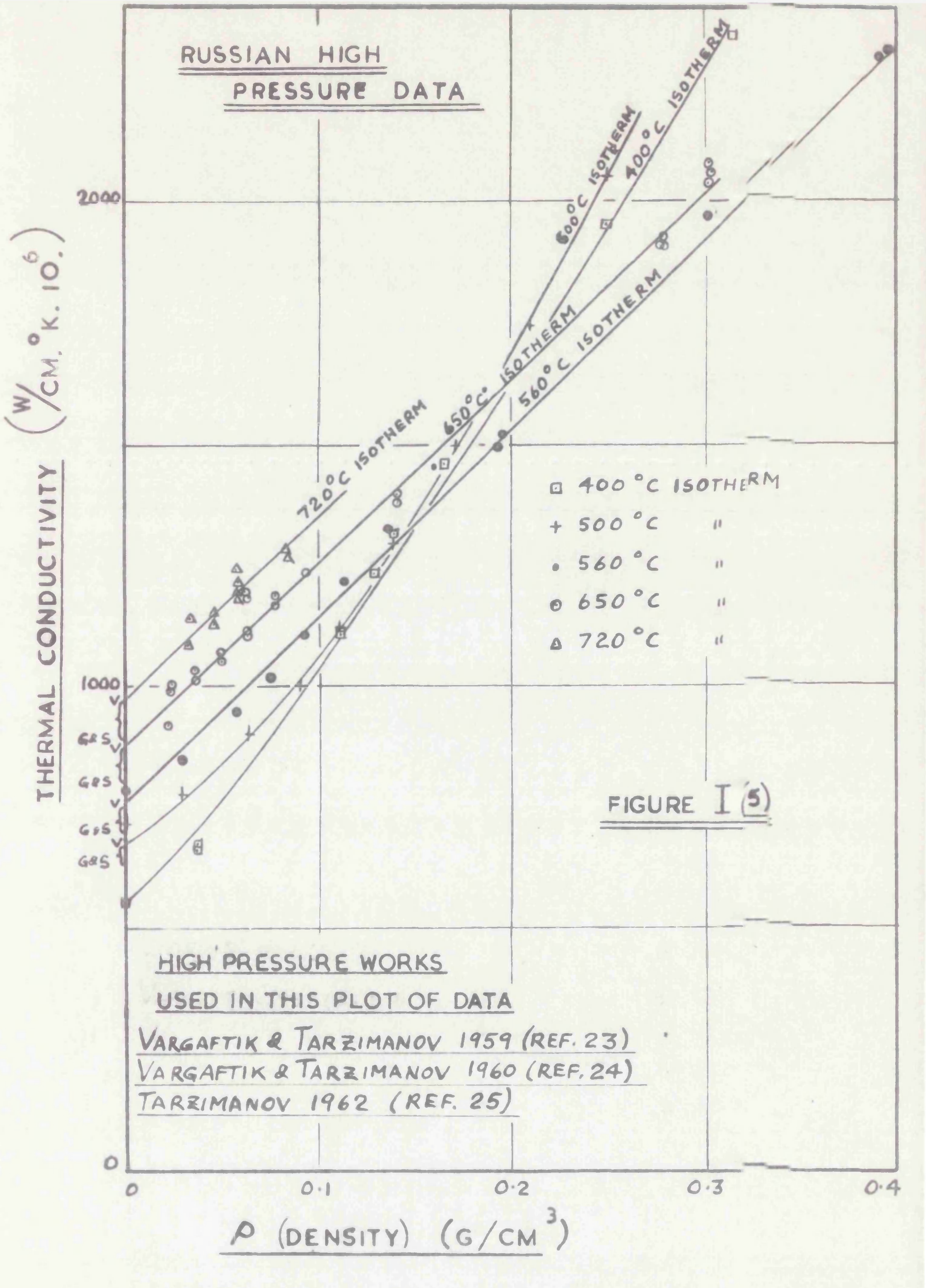

RUSSIAN HIGH PRESSURE DATA
THERMAL CONDUCTIVITY (W/CM. °K. 10^6)
ρ (DENSITY) (G/CM^3)
0
1000
2000
0.1
0.2
0.3
0.4
720°C ISOTHERM
650°C ISOTHERM
560°C ISOTHERM
500°C ISOTHERM
400°C ISOTHERM
V
G&S
400 °C ISOTHERM
+ 500 °C "
• 560 °C "
650 °C "
720 °C "
HIGH PRESSURE WORKS
USED IN THIS PLOT OF DATA
VARGAFTIK & TARZIMANOV 1959 (REF. 23)
VARGAFTIK & TARZIMANOV 1960 (REF. 24)
TARZIMANOV 1962 (REF. 25)

FIGURE I (5)

of Vargaftik and associates.

In order to confirm the Russian observations it was thought essential that remeasurement of the atmospheric line over the temperature range 100°C - 700°C should be undertaken, preferably outside the U.S. and U.S.S.R. It was also hoped that new measurements would help lead to a reduction in the tolerances given for equation I (D) if, in fact, the results did support the Russian values.

CHAPTER II

METHOD OF MEASUREMENT

II (1) Introduction

The equation for the general case of heat conduction in a cube of homogeneous substance of small sides dx, dy and dz.

$$\frac{\lambda}{c\rho}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) = \frac{\partial T}{\partial t} \qquad \ldots \text{II (A)}$$

(where λ is the coefficient of thermal conductivity which may be defined as a physical property of the substance characterising the ability of the substance to transfer heat by conduction; c is the specific heat of the substance; ρ is the density of the substance; T is temperature and t refers to time) is derived from the basic law of heat transfer by conduction originally formulated by Fourier. For conductive heat flow in one direction he stated that "The quantity of heat transferred (Q) is proportional to the temperature gradient $\left(\frac{dT}{dx}\right)$, time (t) and the area of surface normal to the direction of heat flow (A). Expressed in symbols that is

$$q = \frac{Q}{t} = -\lambda A \frac{dT}{dx} \qquad \ldots \text{II (B)}$$

Any apparatus which supplies the necessary boundary conditions for a particular solution to equation II(A) can be used to determine thermal conductivity.

Methods of measuring the thermal conductivity of gases and liquids have been outlined by Venart (27) and given in more detail by Tsederberg (28) in his excellent book. Hence the following survey of methods which were considered need only be brief but should be included for completeness of this text and also so that comparisons between different methods can conveniently be shown when selection of the apparatus thought to be the most suitable for atmospheric steam measurements is made.

II (2) Survey of Methods of Measurement

II (2) (A) Steady State Methods of Measurement

A steady state heat flow method is one in which a time independent temperature field is maintained and heat flow is constant with time. In these methods, by using an apparatus of convenient geometry, heat flow in one direction may be established. The basic equation II (A) is considerably simplified and an accurate knowledge of the density and specific heat values contained in the thermal diffusivity term $\left(\frac{\lambda}{c\rho}\right)$ is not necessary.

Nearly all steam measurements have been made using steady state methods.

Parallel - Plate Apparatus

In this method (see figure II (1)) a sample of test gas is contained in a narrow separation between two horizontal flat plates U.P. and L.P. The upper plate is heated to a uniform overall temperature and heat flows from the upper to the lower plate. When steady state conditions are reached and there is a uniform steady heat flow through the gas layer from the upper plate, at temperature T_1, through the gas layer to the cooler bottom plate, at temperature T_2, neglecting edge effects, the basic equation which may be applied is

$$q = \frac{\lambda A (T_1 - T_2)}{\Delta x} \qquad \text{.... II (C)}$$

By measuring the area normal to heat flow A, the thickness of the test gas layer Δx, the heat flowing by conduction across the gap q and the temperatures of the upper and lower plates T_1 and T_2 the value of thermal conductivity of the gas at average temperature $T_2 + \frac{T_1 - T_2}{2}$ and measured gas pressure may be obtained.

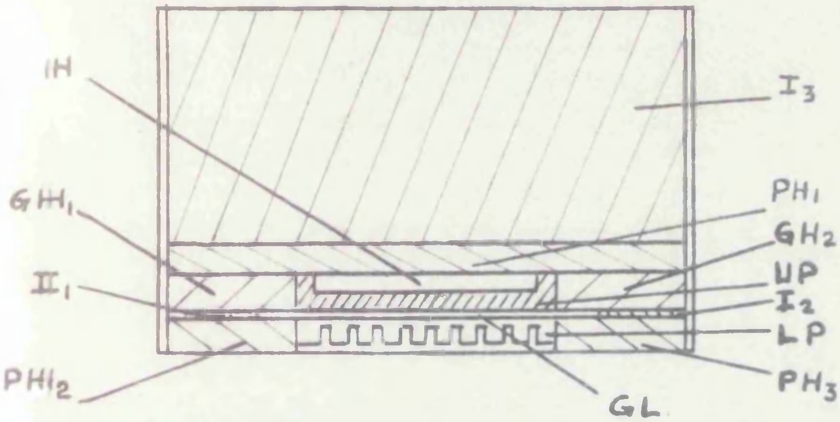
The parallel plate method was first used by Christiansen (29) in 1881. Probably the earliest British experimenter to use this method for measurement of gases was Todd (30). Following these works a number of experimenters improved the apparatus somewhat. A note-able work was that of Hercus and Laby (31) who used 'guard rings' to minimise heat flow from the edges of the plates. Recent experimenters who have successfully employed this method are Nuttall and Ginnings(32) who made measurements on nitrogen in the temperature range $50^{\circ}C - 500^{\circ}C$ and at pressures of 1 to 100 atmospheres and Sengers and Michels (33) who made measurements on carbon dioxide in the critical region.

For steam, measurements in the critical region have recently been obtained by Amirkhanov and Adamov (34) using a parallel plate apparatus.

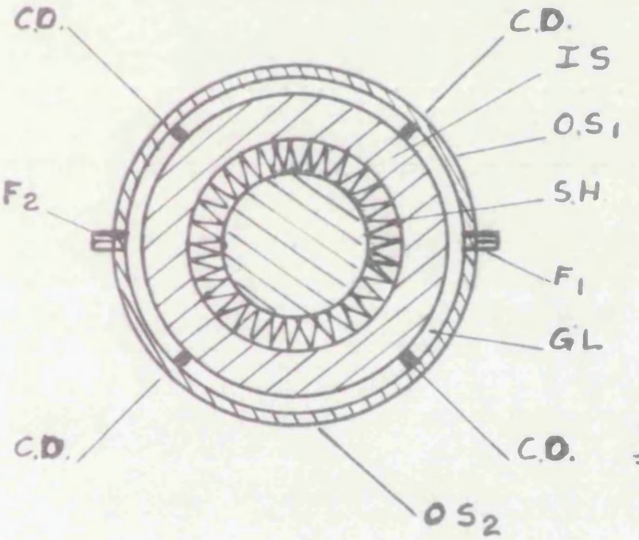
Spherical Apparatus

In this type of cell(see figure II (1)) the test gas is enclosed between two concentric spheres. The inner sphere is uni-

PARALLEL PLATE APPARATUS

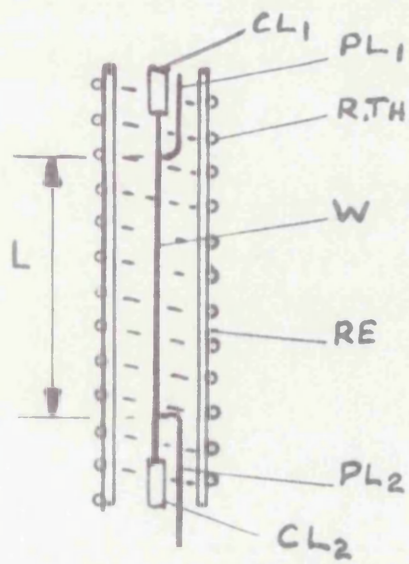


U.P. UPPER HEATER PLATE
L.P. LOWER PLATE
G.L. GAS LAYER
GH_1, GH_2 GUARD HEATERS
PH_1, PH_2, PH_3 PROTECTIVE HEATERS
I_1, I_2, I_3 THERMAL INSULATION
H HEATING COIL FOR UPPER PLATE



IS INNER SPHERE
OS_1, OS_2 OUTER HEMISPHERICAL SHELLS
SH SPHERICAL HEATER
CD CENTERING DEVICES
GL GAS LAYER
F_1, F_2 FLANGES

SPHERICAL APPARATUS



L. LENGTH OF MEASUREMENT SECTION
W. WIRE HEATER
RE. RECEIVER TUBE
CL_1, CL_2. CURRENT LEADS
PL_1, PL_2. POTENTIAL LEADS

R.T H. RECEIVER RESISTANCE THERMOMETER

HOT WIRE APPARATUS

FIGURE II (1)

formly heated and the heat flows through the test gas layer to the outer receiving sphere. By measuring the temperature difference between the inner and outer spheres and the heat flow by conduction across the test gas, when the cell is at steady state conditions and knowing also the diameters of the spheres, the thermal conductivity of the test gas at mean temperature $T_2 + \frac{T_1 - T_2}{2}$ and measured gas pressure may be calculated from

$$q = \frac{\lambda\, 4\pi\, (T_1 - T_2)}{\frac{1}{r_1} - \frac{1}{r_2}} \qquad \text{.... II (D)}$$

(where q is the heat flow by conduction through the test gas layer, T_1 is the temperature of the outer surface of the inner sphere, T_2 is the temperature of the inner surface of the outer sphere, r_1 is the radius of the inner sphere and r_2 is the internal radius of the outer sphere).

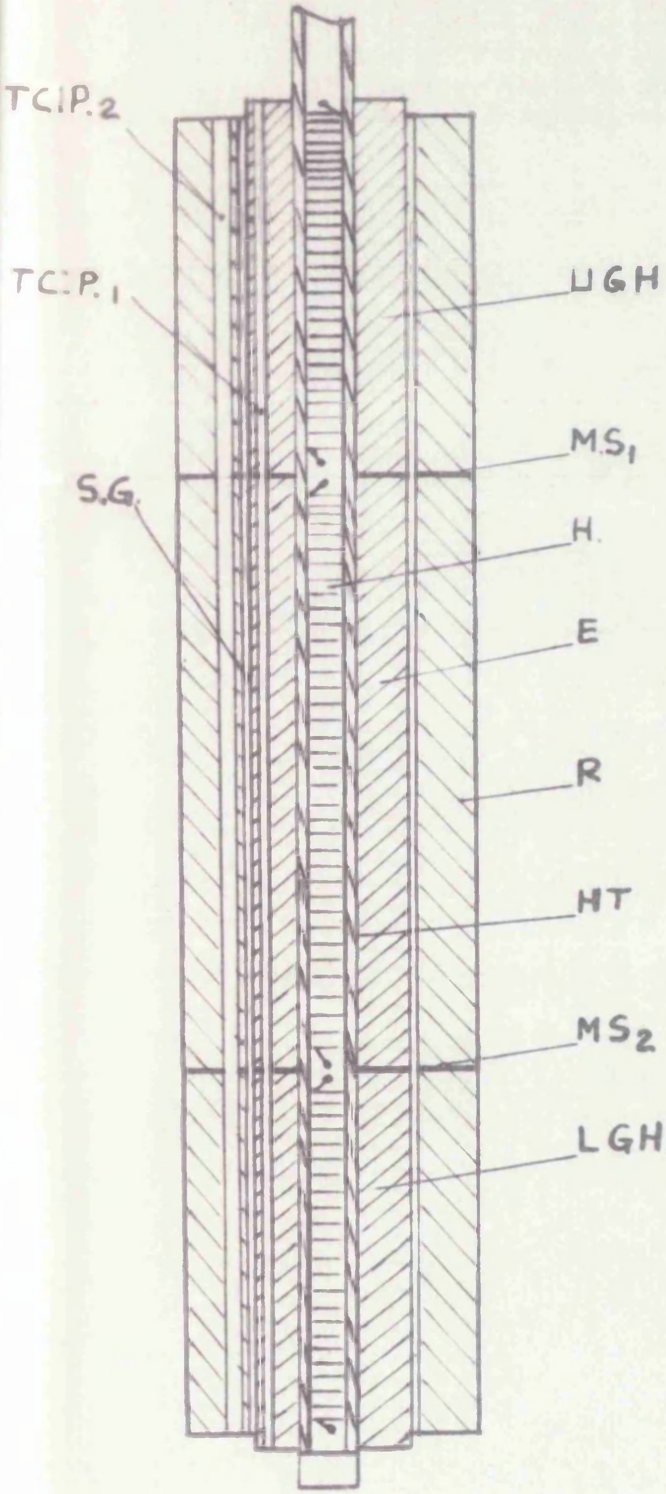
Towards the end of the 19th century experimenters Kundt and Warburg (35) used a spherical apparatus. However, this type of apparatus has not been particularly popular for reasons which will be discussed later. Riedel (36) and more recently Sage (37) are experimenters who have successfully employed this method.

To the best of the author's knowledge this type of cell has never been used to measure steam.

<u>Cylindrical Apparatus</u>

In cells of cylindrical geometry the test gas is enclosed between two vertical concentric cylinders. Heat is generated in the inner cylinder or emitter and conducted radially through the gas filled annulus to the concentric outer receiving cylinder. When steady

VENART'S CONCENTRIC CYLINDER CELL



E	INNER CYLINDER
R	OUTER CYLINDER
UGH	UPPER HEAT GUARD
LGH	LOWER HEAT GUARD
H	ELECTRICAL HEATER
HT	S.S HEATER TUBE
MS_1, MS_2	MICA SPACERS
SG	STEAM GAP
TCP_1, TCP_2	THERMOCOUPLE POCKETS

FIGURE II(2)

state conditions are reached the basic equation which may be applied to obtain the thermal conductivity of the gas λ at mean temperature $T_2 + \frac{T_1 - T_2}{2}$ and measured gas pressure is, neglecting edge effects,

$$q = \frac{\lambda \, 2\pi L \, (T_1 - T_2)}{\log_e \frac{r_2}{r_1}} \qquad \text{.... II (E)}$$

By measuring the heat being conducted radially q, the surface temperatures of the inner and outer cylinders T_1 and T_2, the radius of the inner cylinder r_1, the internal radius of the outer cylinder r_2 and the length of the emitter measurement section L, the thermal conductivity of the test gas may be calculated.

The two main types of cell of cylindrical geometry which have been previously used may be listed under the headings (1) Concentric cylinder cells and (2) Hot Wire cells.

(1) <u>Concentric Cylinder Cells</u>

In this cell the emitter is a thick cylinder (see figure II (2)) and the gas annulus used is of very small width compared to the diameter of this cylinder.

Since 1874 various configurations of this type of cell have been used for measurements on both liquids and gases. Among the earlier experimenters who used this method was Sellschopp (38) who was probably the first to measure CO_2 over a wide range of pressures. Experiments performed by Keyes, such as those described in reference (39) have helped to make this method of measurement popular in the United States of America. Some of the more recent experimenters who have obtained good results for gases are Ziebland et al (40), (41), (42), Rothman (43) and Guildner (44).

For steam as was stated in chapter I workers who have used this type of cell are Vargaftik and Smirnova (11), Keyes and Sandell (9), Keyes and Vines (10), Vines (12) and Venart (1).

(2) Hot Wire Cells

In this method (see figure II (1)) the emitter is a small diameter wire, usually of the order of 0.1 mm diameter, coaxially centered in a receiver which is generally a thin tube made of quartz or glass. For work at high pressures very narrow bore tubes (typical value 0.8 mm) must be used. For work at near atmospheric pressure bore sizes as large as 8 mm bore have been used. The wire is both a heater and resistance thermometer.

This method was first used effectively by Schleiermacher (3) in 1888 and has been used extensively for gas thermal conductivity measurements since then. Following this work a particularly important modification of the apparatus was carried out by several experimenters. By using two cells, identical except in length and subtracting the results obtained the effects of end conduction were accounted for. Weber (45) was among the earlier experimenters who utilised this improvement. Further improvements were carried out in Britain by Gregory et al (46), (47), (48), (49), (50), (51). This considerable work helped to increase the popularity of this method.

For steam at atmospheric pressure as was again stated in chapter I the workers Moser (2), Milverton (4), Vargaftik (5), Vargaftik and Oleshchuk (17), Vargaftik (8), Vargaftik and Smirnova (11), Geier and Schafer (13), and Vargaftik and Zimina (14) have used this method.

II (2) (B) Other Methods of Measurement

In addition to steady state methods transient methods and indirect determination methods are ways in which the thermal conductivity of steam may be determined.

In transient methods an unsteady state process takes place in which the temperature field changes with time. Methods of this type were not rigorously considered for the proposed measurements on steam. The purpose of these measurements, which was to confirm or reject Russian values, made it necessary that a basic method which had been well tried and tested for steam over the years should be used. To the author's knowledge only one work, the recent publication of Vukalovich and Cherneeva (52) has been performed for steam using a transient method. This most interesting method which they used was based on "Kondrat'ev's regular regime" principles. The cell which they used was a concentric cylinder cell with guard heating applied to both ends. A description of the "regular regime" method may be found in reference (28). The results which Vukalovich and Cherneeva obtained indicate that this method is most promising but the deviation of their results at a pressure of 500 atmospheres from the results of Vargaftik and Tarzimanov (23),(24),(25) is 6%. For water Gillan and Lamn (53) have used a transient method to obtain results with an estimated accuracy of $\pm$ 1%.

In indirect determinations, a function which contains the thermal conductivity as one of its variables (e.g. Prandtl number) is measured and by substituting the values of the other variables the thermal conductivity may be obtained. Such methods were not considered as suitable as absolute steady state methods, for measurement on steam.

II (3) Selection of Test Cell

For the reason already stated it was decided that a steady state method of measurement should be used. It was also concluded that an absolute method was best since calibration of the cell with a gas of known conductivity is less accurate than calculation of the cell constant from careful, accurate, measurement of the cell dimensions. For instance, the values of the thermal conductivity of the gas with probably the most accurately known values, argon, could be subject to an error of $\pm$ 1%.

The choice of cell with the most suitable geometry was then made. A spherical type of cell was first studied. Initially it appeared that this shape was most satisfactory. Since no guard heating was required it seemed that equation II (D) could be applied without modifications.

This type of apparatus was, however, rejected for several reasons. It is difficult to construct a spherical heater to produce a uniform heat flux. The problems of bringingout the heater leads and of centering the inner sphere without appreciably disturbing symmetry are difficult. The sphere must be accurately centered along both axes of symmetry since no advantage is to be gained if the sphere is centered along one axis and there is eccentricity at the other axis. In obtaining a symmetrical continuous internal surface in the receiver serious problems are encountered not only in machining but also in arranging that the cell can be filled and evacuated when necessary.

The parallel plate type of cell was next studied. From examination of equations II (C) and II (E) it can be seen that since in the concentric cylinder cell the gap size is very small compared to the radius of the emitter, virtually the same equation holds for both methods. The parallel plate method utilises a cell of the simplest geometry and by applying a downward heat flow across the narrow gas gap theory shows that convective heat flow is eliminated.

This method was finally rejected for the following reasons. Maintaining the temperature at a constant value over the surface of the plate is more difficult than in a cell of cylindrical geometry. Instability of the flat plate cell alignment affects the cell constant directly but a change in coaxial cylinder cell alignment affects the cell constant comparatively little. In order to provide accurate measurement of heat flow through the gas gap the apparatus must be guarded on both top and sides. In addition the thermostat in which the cell is to be enclosed is awkward to construct.

The choice was now limited to cells of cylindrical geometry. Both hot wire and concentric cylinder cells have been widely used with undoubted success. For the measurement of steam at atmospheric pressure

THE CELL OF KEYES AND VINES

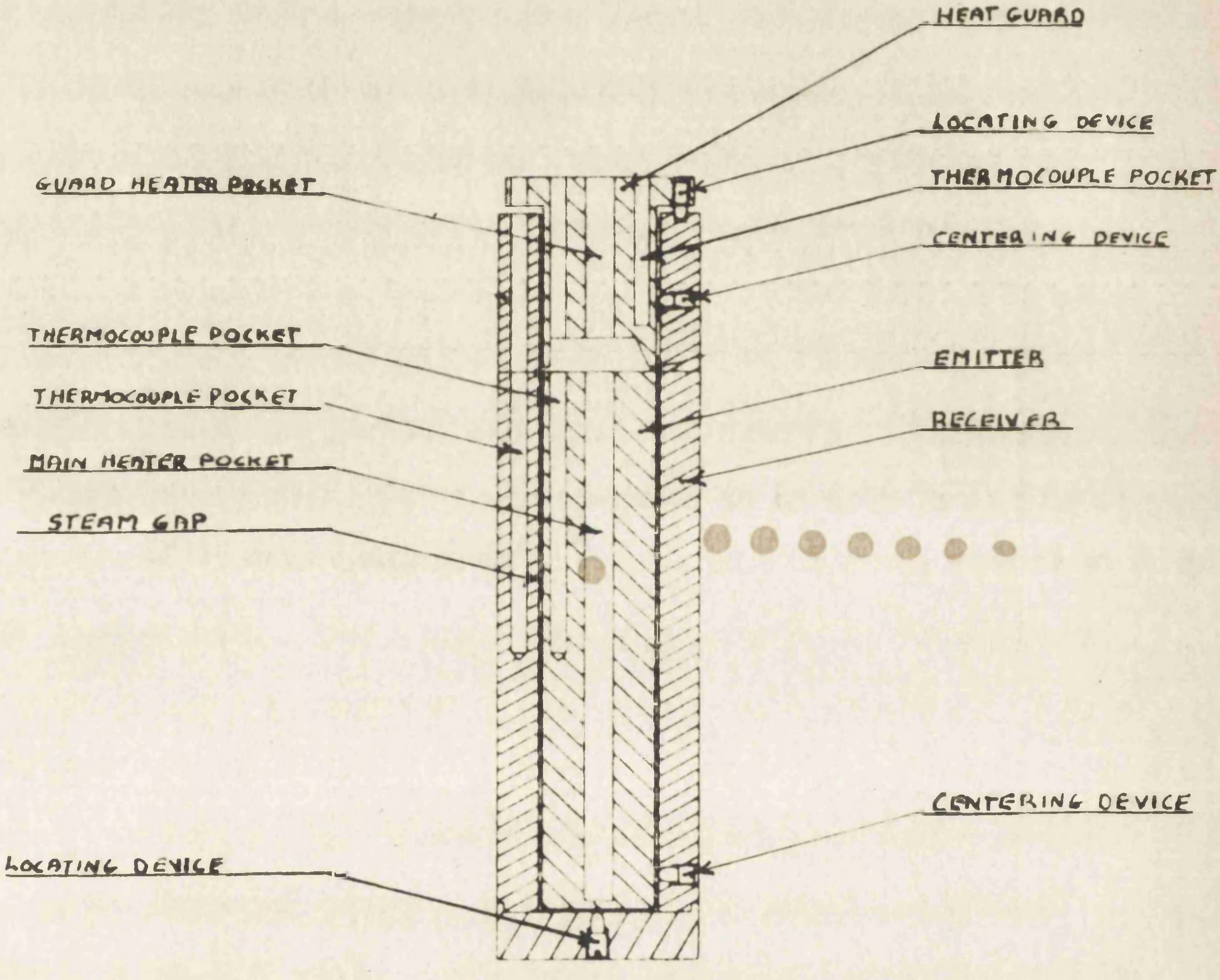


FIGURE II(3)

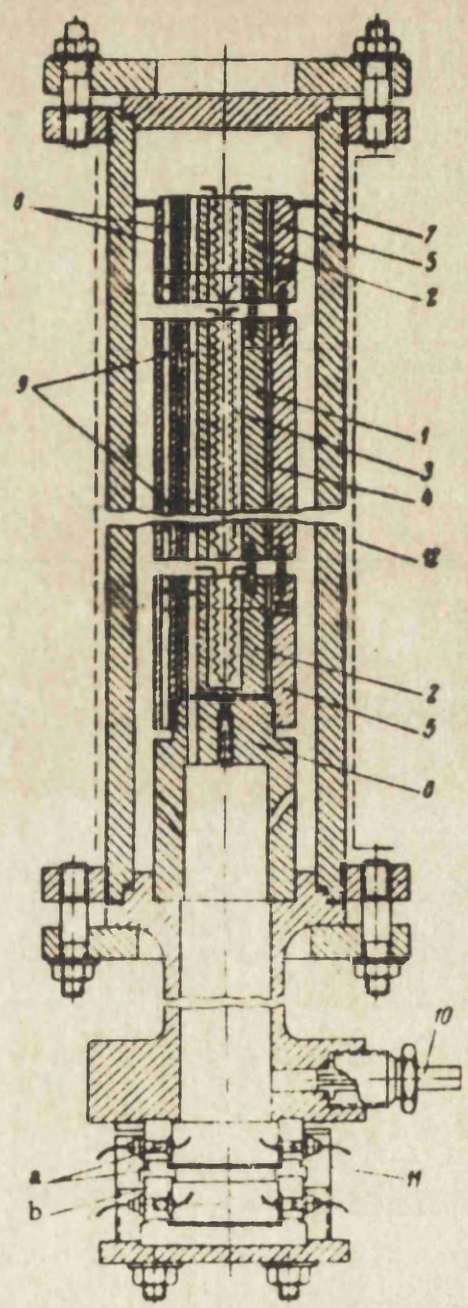
the merits of both methods are fairly evenly balanced.

In the hot wire cells lack of temperature uniformity along the length of the wire poses a problem. It is more difficult to line up the wire coaxially inside the receiver than it is to centre the emitter in a concentric cylinder cell. In order to keep the ratio of heat radiated to heat conducted across the gas gap small, as well as eliminating significant convection, a fine wire and a narrow bore tube must be used. The wire is, of course, both a heater and a resistance thermometer and must be carefully suspended to avoid strains due to thermal expansion since the resistance of the wire changes substantially when it is strained. It is most difficult when a fine wire is used to keep the necessarily small annular space between emitter and receiver and still keep the wire free from strain. The reasonably high emissivity of the platinum wire also serves to increase the correction to be applied for radiation.

A cell of the concentric cylinder type was finally chosen. As stated above the accurate centering of the emitter is easier than in a hot wire cell. Independent temperature measuring devices, such as thermocouples, can be used. There is no need to calibrate and recalibrate the wire forming the electrical heater in the emitter. In addition by choosing a cell material of low emissivity and using a small gas gap, the ratio of heat radiated to heat conducted can be made extremely small.

Having decided to use a concentric cylinder type of cell it was noted that various configurations of this type of cell had been

THE CELL OF VARGAFTIK AND SMIRNOVA



Drawing of instrument for measuring thermal conductivity of water vapor (method of coaxial cylinders).
1) Inside measuring cylinder; 2) protective cylinders;
3) electrical heater; 4) external measuring cylinder;
5) protective external cylinders; 6) metallic plug;
7) mica ring; 8) channels for thermocouples;
9) thermocouples (indicated by dots); 10) sleeve for introduction of gas investigated; 11) stack of rings for bringing leads out of the equipment: a) copper, b) plexiglass; 12) electrical heater thermostat.

FIGURE I(4)

VINES' CELL

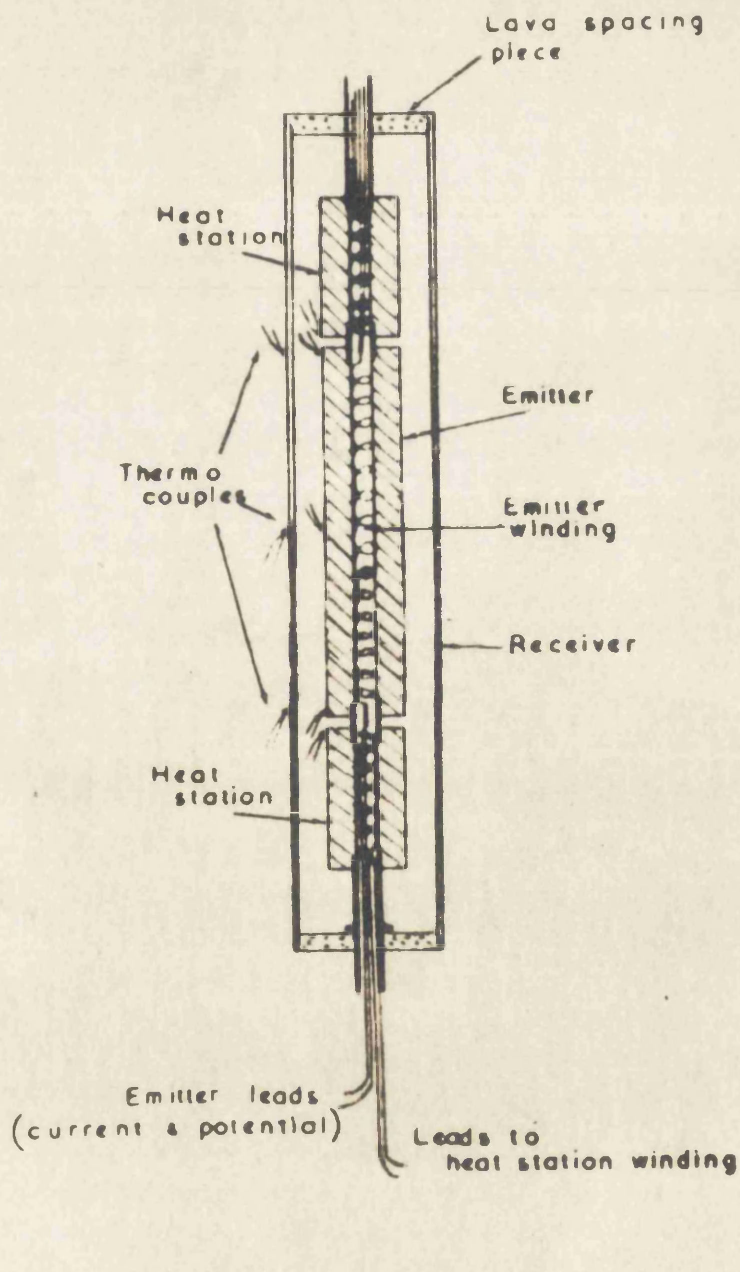


FIGURE II(5)

used. For steam Keyes and Sandell (9) and Keyes and Vines (10) have used cells with guard heaters at one end only (see figure II (3)). In this type of cell the basic equation used for conductivity determinations is

$$q = \frac{2\pi L \lambda \Delta T}{\log_e \frac{r_2}{r_1}} + \frac{\pi r_1^2 \lambda \Delta T}{x} + q_{CORNER} \quad \text{.... II(F)}$$

(where q = heat input to the emitter, λ = thermal conductivity of steam, ΔT = temperature difference between emitter and receiver, r_1 and r_2 are the radii of emitter and receiver respectively, x = the width of the gap at the bottom of the cell, L = the length of the emitter and q_{CORNER} = the term added to the heat flow due to the bottom corner).

Corrections have to be applied to this equation to take into account the asymmetric temperature distribution in the emitter. The main objection to a cell of this type is that calculation of the heat flow from the emitter across the support pins is complicated. Apart from an approximate mathematical solution the effect of this conduction can be taken into account in two ways (a) By performing measurements at high vacuum or (b) By calibrating the cell with a gas of known conductivity.

Novel types of concentric cylinder cells have been constructed by Johannin (54) who has made measurements on gases and Leidenfrost (55) with which it is hoped he will measure steam to 500°C.

A cell with guard heaters at both ends such as those used by Vargaftik and Smirnova (11), Vines (12) (see figures II (4) and II (5)) and Venart (1) was eventually selected. This type of cell gives the closest approximation to the basic Fourier equation. The centering devices may be located well away from the measurement section. It is conceded, however, that accurate control of the guard heaters increases the time taken to obtain measurements.

II (4) SOME OF THE MORE IMPORTANT FACTORS WHICH MUST BE CONSIDERED FOR ACCURATE MEASUREMENT

So that the basic equation may be used accurately there are certain important factors which must be taken into consideration and understood before starting experimental work.

As stated before the basic Fourier equation is

$$\lambda = \frac{\log_e \frac{r_2}{r_1}}{2\pi L} \cdot \frac{q}{\Delta T} \qquad \text{.... II (E)}$$

or

$$\lambda = K \cdot \frac{q}{\Delta T}$$

where K is termed the cell constant.

Factors affecting the cell constant, heat input and temperature difference will be considered separately.

II (4) (A) Factors affecting temperature difference measurement. The Temperature drop in the cell material

So that symmetry in the gap separating the two cylinders may be maintained the thermocouples or resistance thermometers to be used for temperature measurement must be located below the cylindrical surfaces of the cell components. When the apparatus is at steady state conditions and heat is flowing radially, small temperature differences will exist between the walls of the cylinders and the thermocouples. These small differences must be taken into account if the temperature difference across the gas annulus is to be accurately known. By knowing the exact position of the thermocouples, r_i and r_o, the thermal conductivity of the test cell material λ_{s1}, the measured heat flow q, and the cell emitter and receiver radii, r_1 and r_2 respectively, the cell length L and assuming the total heat input is conducted across the steam gap, the effects of the temperature drops in the cell material may be taken into account by altering equation II (E) to

$$\lambda = \frac{q \lambda_{s1} \log_e \frac{r_2}{r_1}}{2\pi L \Delta T \lambda_{s1} - q\left(\log_e \frac{r_o}{r_2} + \log_e \frac{r_1}{r_i}\right)} \qquad \text{..... II (G)}$$

where ΔT is the measured temperature difference.

The Effects of Temperature Discontinuity

In thermal conductivity measurements the temperature drop in the test gas layer is assumed to be the temperature difference between the surfaces of the emitter and cooler receiver. It is true, however, that the gas layer, one mean free path away from, say, the receiver wall, will be hotter than the receiver surface even assuming that the gas molecules striking the metal surface attain the temperature of the metal. Similarly the gas layer one mean free path away from the surface of the emitter will be cooler than the emitter surface. In addition all the gas molecules reaching the cell surfaces do not attain the temperatures of the cell surfaces. Hence molecules at a temperature T striking at hot surface at temperature T_1 will leave the surface at a temperature T' which is less than T_1 and related to it by

$$T' - T = a(T_1 - T) \qquad \text{.... II (H)}$$

where a is termed the accommodation coefficient of the gas with respect to the cell surface.

At high pressures the effects of this 'temperature jump' at the cell surfaces is negligible as the mean free path of the gas molecules is very small compared to the dimensions of the gas gap. At low pressures (several tens of mm Hg or lower) especially at high temperatures when the length of the mean free path is comparable with the dimensions of the gas gap the effect of this jump in temperature can be very significant.

It can be shown that the 'temperature jump' at a solid rarefied gas boundary is proportional to the temperature gradient and inversely proportional to pressure.

$$T_H - T' = -\frac{A_1}{p}\left(\frac{dT}{dx}\right)_{x=x_1}$$

and $$T'' - T_c = -\frac{A_2}{p}\left(\frac{dT}{dx}\right)_{x=x_2}$$

(where T_H, T_c = temperatures of "hot" and "cold" surfaces

T', T'' = temperatures of gas at "hot" and "cold" surfaces

A_1, A_2 = Coefficients of proportionality

p = gas pressure

For a concentric cylinder apparatus

$$\left(\frac{dT}{dx}\right)_{x=x_1} = -\frac{q}{\lambda\, 2\pi r_1 L}$$

$$\left(\frac{dT}{dx}\right)_{x=x_2} = -\frac{q}{\lambda\, 2\pi r_2 L}$$

Hence

$$T_H - T_c = (T' - T'') + \frac{q}{\lambda 2\pi L}\left(\frac{A_1}{r_1} + \frac{A_2}{r_2}\right)\frac{1}{p}$$

$$\therefore \quad \Delta T_{MEAS.} = \Delta T_g + \beta \cdot \frac{1}{p}$$

If a series of experiments are carried out at different low pressures and the measured ΔT plotted against $\frac{1}{p}$ by extrapolating the line to $\frac{1}{p} = 0$. ΔT_g can be found and substituted in the Fourier equation.

Vargaftik and Zimina (21) have derived an excellent means by which the influence of thermal jump in one set of experiments may be calculated using the experiments of other workers. They have shown that the ratio of the percentage corrections for temperature discontinuity to be applied to the measured temperature difference in two hot wire instruments, in which the accommodation coefficients of the gas with respect to the wires is the same, measuring the same gas, at the same temperature and pressure, can be estimated to be

$$\frac{e_1}{e_2} = \frac{\%\ \text{error in temperature difference in cell}_1}{\%\ \text{error in temperature difference in cell}_2}$$

$$= \frac{r_2 \log_e \frac{R_2}{r_2}}{r_1 \log_e \frac{R_1}{r_1}}$$

where r is the radius of the wire

R is the internal radius of the receiver.

For two concentric cylinder cells

$$\frac{e_1}{e_2} = \frac{\delta_2}{\delta_1}$$

where δ is the cylindrical gas gap width

For a hot wire cell and a concentric cylinder cell

$$\frac{e_1}{e_2} = \frac{2 r_2 \log_e \frac{R_2}{r_2}}{\delta_1}$$

II (4) (B) Factors Affecting Measured Value of Radial Heat Flow Axial Heat Flow

Since the emitter measurement section is of finite length some of the heat input will tend to flow axially as well as radially. The problem of combined axial and radial conduction in a cylindrical emitter has been studied by Jacob (56). He has shown that if the temperatures at the ends of the emitter are equally out of balance with the temperature at the centre of the emitter, the equation

$$\frac{d^2\theta}{dx^2} = \frac{\lambda\, 2\pi}{(\lambda_s A)_a \log_e \frac{r_2}{r_1}} \cdot \theta - \frac{q}{2L(\lambda_s A)_a} \qquad \text{.... II (J)}$$

(where θ is the temperature difference across the gas gap, x refers to axial distance from the emitter centre, λ is the thermal conductivity of the test gas, r_2 is the internal radius of the receiver, r_1 is the radius of the emitter, $(\lambda_s A)_a$ is the axial conductance of the emitter, $2L$ is the emitter length and q is the heat input to the emitter), can be used to determine λ.

Flynn (57) in his work on measuring the thermal conductivity of powder insulating materials has also given a solution to this problem. In his solution he takes into account asymmetric temperature distribution along the length of the emitter and also takes into account the variation of electric heater wire resistance with temperature.

A very accurate solution to the problem of the influence of axial heat flow on thermal conductivity measurements in a concentric cylinder cell can prove to be difficult. Easily the best way is to evaluate the influence is experimentally. An experimental method will be described later. Experiments should, of course, be designed such that any axial heat flow will be extremely small. This can be done in three ways. Firstly, by making the gaps between the emitter and guard cylinders of low conductance. Secondly, by accurately matching the temperature of the heat guards with the temperature at the centre of the emitter and thirdly, by using reasonably large heat inputs to the central heater.

Convection

In a vertical concentric cylinder apparatus convective heat flow will always be present. Indeed the only type of cell in which convection, theoretically at least, will not be present is the parallel plate cell with downward heat flow. It has, however, been shown that for very slow "creeping motions" heat is still transferred through the fluid layer of conduction alone.

For natural convection, heat flow from the surface of the emitter is a function of characteristic dimension l, temperature difference ΔT, thermal conductivity λ, absolute viscosity of fluid μ, specific heat of fluid C_p, coefficient of volumetric expansion α, acceleration due to gravity g and the density of the fluid ρ. By using dimensional analysis it can be shown that if h is the heat transferred from the emitter surface in unit time per unit area.

$$\frac{h\,l}{\lambda\,\Delta T} \text{ is a function of } \left(\frac{\mu C_p}{\lambda}\right)\left(\frac{\alpha g\,\Delta T\,l^3\rho^2}{\mu^2}\right)$$

(Nusselt number) = f (Prandtl number). (Grashof number)

for a concentric cylinder apparatus where $\frac{r_2}{r_1} \doteqdot 1$ the characteristic dimension used is δ (the gap size). The Nusselt number is then

$$\frac{h}{\frac{\lambda \Delta T}{\delta}} \text{ or } \frac{h}{q}$$

where q is the heat transferred/unit time, unit area by conduction.

In analysing data for heat flow between concentric cylinders where the ratio of the receiver radius to the emitter radius is small, Kraussold (60) plotted the Nusselt number against log (Gr. Pr) and found that for

$$Gr.\,Pr. < 1000$$

$h = 9$. This was taken as showing that for cells of this type below Gr.Pr.= 1000 heat flow by convection is very small compared to heat flow by conduction. Except for regions near the saturation line and at the critical point this product is generally used for concentric cylinder cells, to test what influence can be expected from convection effects. Tsederberg (28) has suggested that a safer limit would be Gr.Pr. < 700 under the worst possible conditions.

Radiation

The problem of the influence of thermal radiation on thermal conductivity measurements is one which must be closely considered. Particularly when the gas or vapour filling the annulus between emitter and receiver is an emitting and absorbing medium such as steam.

Since steam is only partially transparent to thermal radiation in the general case radiation will affect heat transfer in two ways. Firstly, as in the case of transparent gases with symmetrical molecules such as hydrogen, nitrogen, oxygen and argon, radiant energy is emitted and absorbed by the cell surfaces. Secondly radiation is emitted and absorbed by the steam, thus altering the temperature distribution such that the gradient is steepest near the cell walls and smallest at points in between (see figure II (6)).

Exact analysis of the problem of combined conduction and radiation is complex. Radiation is emitted and absorbed by the steam only for certain different characteristic bands of wavelength and the wavelength limits of the bands are not exactly known. The radiation emitted per unit volume in unit time in any given band varies with wavelength and the absorbtivity of the steam may depend not only on the temperature of the steam but also on the temperature of the surface from which radiation was first emitted.

The evaluation of combined conduction and radiation involves a highly complex integro-differential equation. Leidenfrost (55)with the aid of mathematician, Viskanta, has tackled this problem. For heat transfer in a steam layer enclosed between two infinite parallel plates Leidenfrost, making several simplifying assumptions, has calculated the radiative flux from the warmer plate into the test medium. Poltz (59) has also tackled this problem and shown how the actual radiative component can be calculated for either diffuse or regular reflections at the cell walls.

In this section it is proposed, firstly, to examine ways in which the radiative heat component may be reduced in the conductivity cell and secondly, to examine how well the usual procedure of calculating the effect of radiant energy exchange by assuming that the test fluid is transparent compares with the exact approach for the range of absorptivities of steam to be covered by this experimental work. This second consideration is of particular importance since previous workers using concentric cylinder cells for steam measurements have not tackled the radiant heat problem by using the exact approach but have assumed that the 'transparent' correction was accurate enough.

For the case of a concentric cylinder apparatus with a narrow gap separating the emitter and the receiver where the gap size is small compared to the diameter of the emitter, radiant heat exchange may be evaluated by assuming heat transfer to take place between two parallel plates. If $T_1 \doteqdot T_2$ (where T_1 and T_2 are the absolute temperatures of the emitter and the receiver respectively) and the radiative component is small compared to the conductive component it has been shown by both Poltz and Leidenfrost that the assumption that the temperature profile between the plates is linear can still be made. It can also be shown that the conductive component is the same whether there is a radiative component or not.

From the work of Poltz (see figure II (6))

$$q_{TOTAL} = \bar{q}_\lambda + \bar{q}_r = \frac{\lambda}{x_o}\int_0^{x_o}\frac{dT}{dx}.dx + \frac{1}{x_o}\int_0^{x_o} q_r\, dx$$
$$= \frac{\lambda}{x_o}(T_1 - T_2) + \frac{1}{x_o}\int_0^{x_o} q_r . dx$$

(where q total = heat input to emitter, $\bar{q}_\lambda$ and $\bar{q}_r$ are the mean conductive and radiative components, λ = the thermal conductivity of the test fluid and x_o = the gap width).

The radiative component is, however, influenced by the conductive component. Simpler approximations to calculate the magnitude of the radiative component do not take into account the effect of conduction on the radiative component and this can in certain cases cause large errors.

Poltz has shown that the radiative component may be calculated from (for steady state conditions)

$$\bar{q}_r = \frac{16}{3}\frac{n^2\sigma T^3\Delta T}{\tau} f(\epsilon, \tau) \qquad \text{... II (K)}$$

TEMPERATURE PROFILES IN STEAM GAP

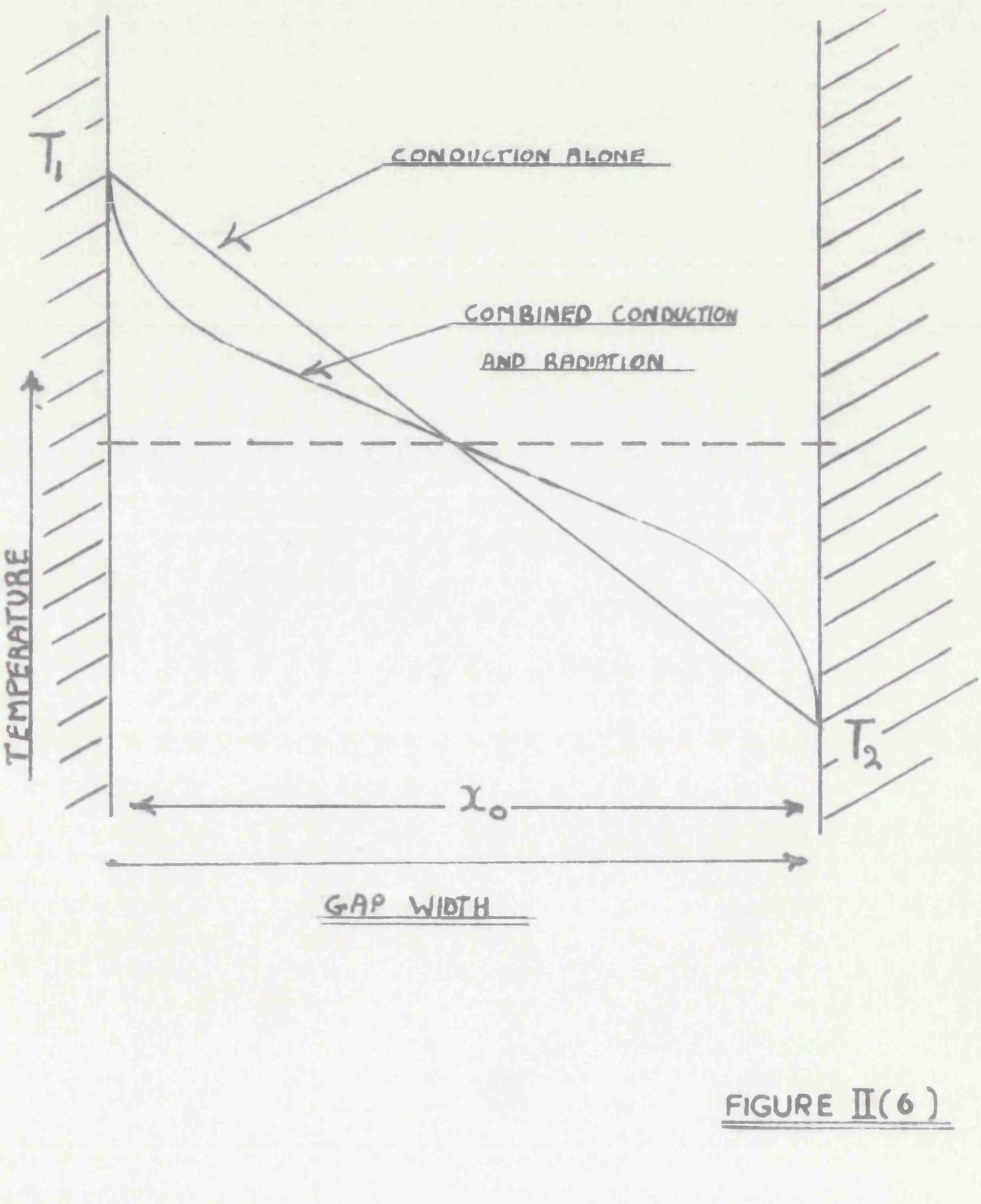


FIGURE II(6)

(where σ = the Stefan-Boltzman constant, n = index of refraction of the test fluid, T = the mean temperature of the test fluid, $\Delta T = T_1 - T_2$, τ = the optical thickness of the test fluid layer and $f(\epsilon, \tau)$ = a function dependant on the emissivity of the cell walls and the optical thickness of the test fluid layer).

For heat radiated through a transparent gas enclosed in a concentric cylinder cell, assuming that the cylindrical surfaces are gray, the ratio of the heat radiated to heat conducted under steady state conditions is

$$\frac{q_r}{q_\lambda} = \frac{\sigma\, n^2\, 2\pi r_1 L\, (T_1^4 - T_2^4)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)} \cdot \frac{\log_e \frac{r_2}{r_1}}{\lambda\, 2\pi L (T_1 - T_2)} \quad \text{.... II (L)}$$

(where r_1 = radius of emitter, r_2 = radius of receiver, L = length of measurement section and ϵ = emissivity of cell surfaces).

From this it can clearly be seen that the radiative component will be reduced by using a cell with surfaces of low emissivity. The conductive component will be increased by using a very narrow gap while the effect of narrowing the gap will have little effect on the radiative component in this case.

For the case of an emitting and absorbing medium it would seem obvious that for a given temperature and optical thickness the radiative component will be reduced by using cell walls of low emissivity, except for very large optical thicknesses where the heat transmitted by radiation through the test fluid will be very small and the influence of the emissivity of the cell walls becomes less

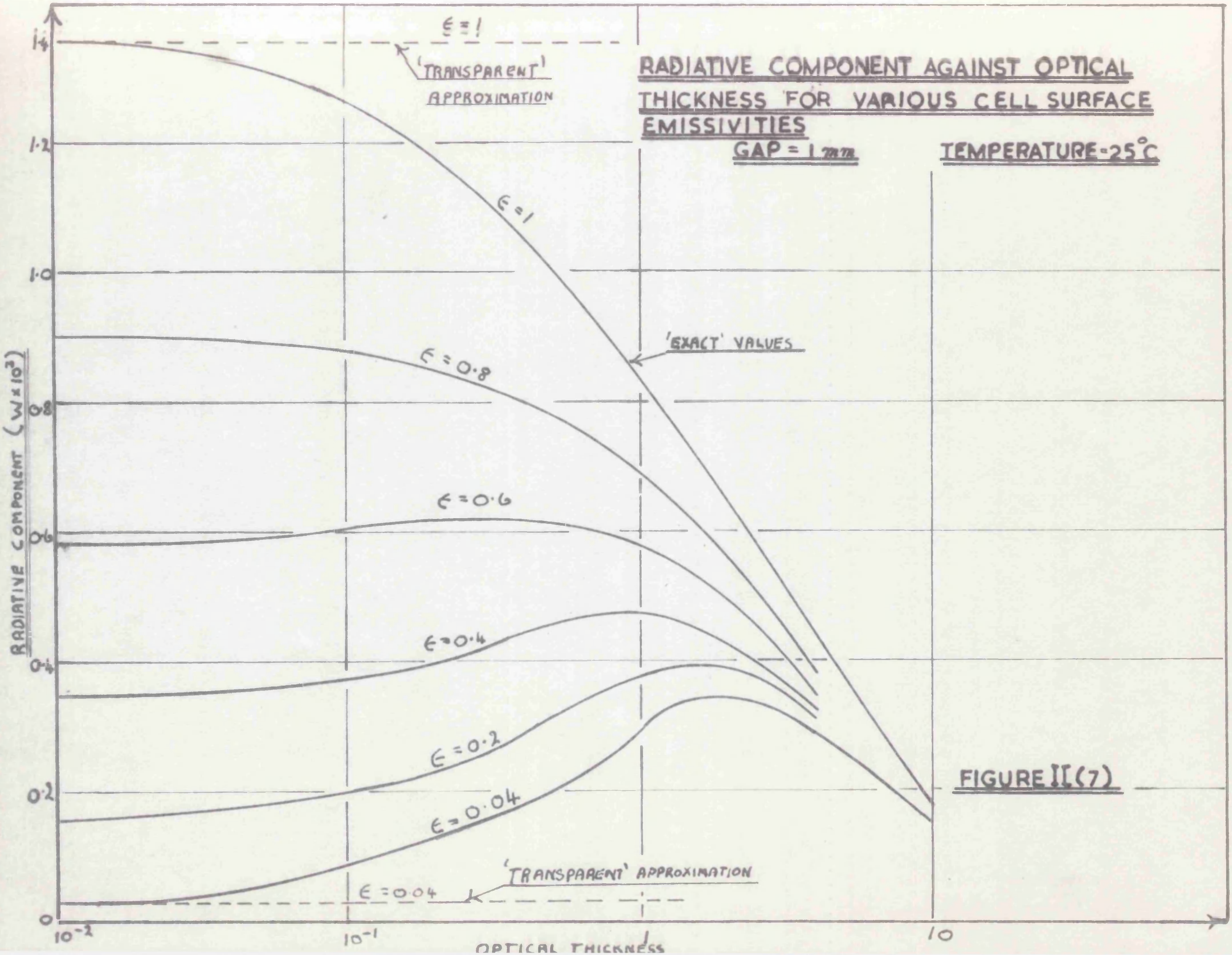
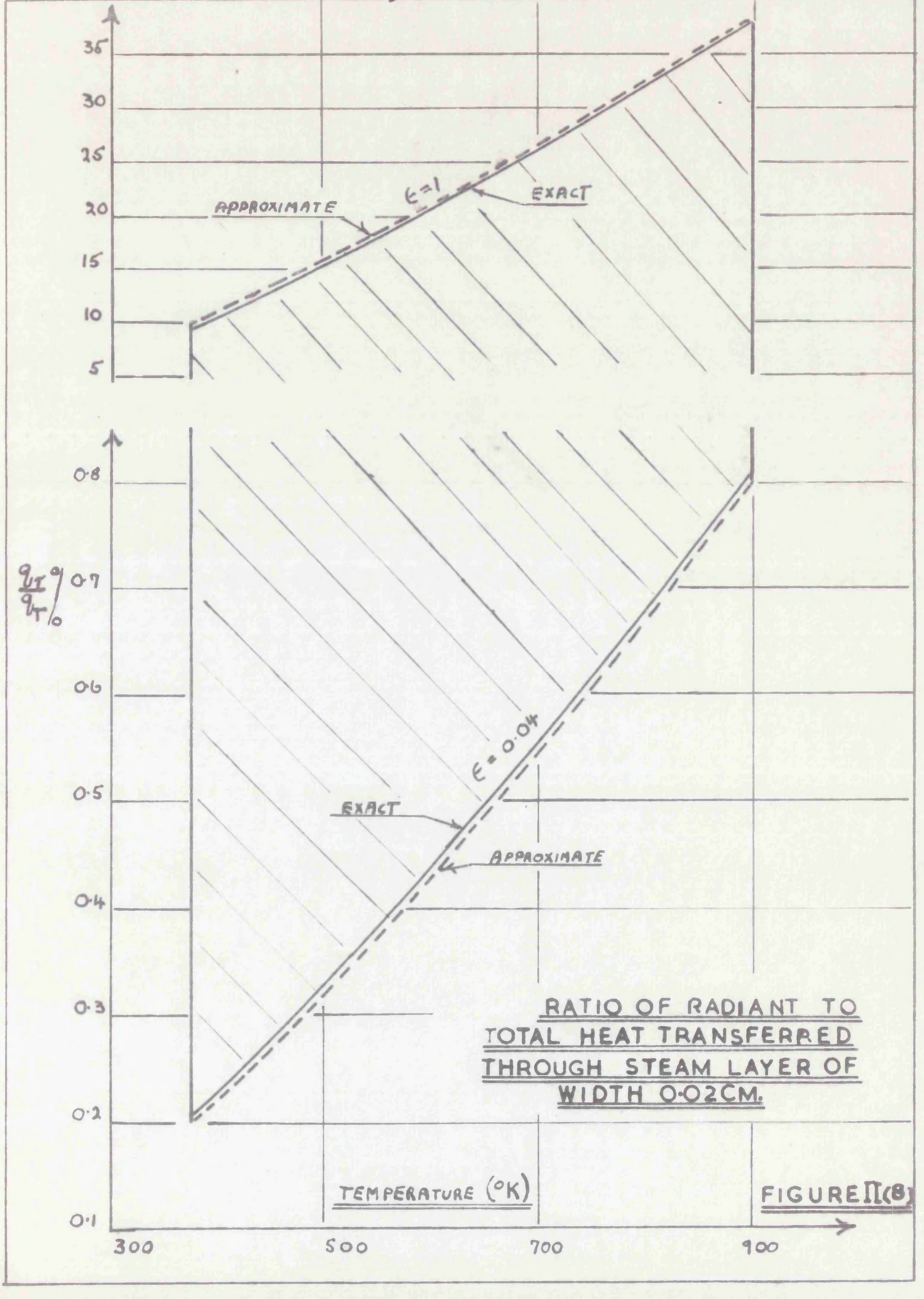

RADIATIVE COMPONENT AGAINST OPTICAL THICKNESS FOR VARIOUS CELL SURFACE EMISSIVITIES
GAP = 1 mm
TEMPERATURE - 25°C
ε = 1
'TRANSPARENT' APPROXIMATION
ε = 1
'EXACT' VALUES
ε = 0.8
ε = 0.6
ε = 0.4
ε = 0.2
ε = 0.04
'TRANSPARENT' APPROXIMATION
ε = 0.04
RADIATIVE COMPONENT (W × 10²)
OPTICAL THICKNESS
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
10⁻²
10⁻¹
1
10

FIGURE II (7)

important. The effect of reducing the gap size is, however, not apparent. At first sight it would appear that to reduce the gap would cause the radiative component as well as the conductive component to increase since the optical thickness is reduced with reducing gap size and the test fluid layer becomes more transparent to radiation.

However, Poltz has shown that for surfaces of low emissivity where the temperature distribution across the gap is controlled almost solely by the conductive component then,due to the effect of this temperature distribution,the radiative component at first increases with increasing optical thickness before reducing. It is true, of course, that were there no conductive component the radiative component should always decrease with increasing optical thickness. In figure II (7) the variation of the radiative component against optical thickness for various valuesof cell surface emissivity is shown. These values were taken from the work of Poltz and refer to a test fluid, index of refraction 1.5 enclosed in a gap of width 1 mm at a temperature of 25^{o}C. From this figure it will be noted that,except for very large optical thicknesses, using a cell with walls of low emissivity effectively reduces the radiant heat component for a given temperature and optical thickness of test fluid layer. It can also be stated that for cells with surfaces of low emissivity enclosing a fluid layer of small optical thickness, which is the general case for gases and vapours, particularly at low pressures and high temperatures, reduction of the gap



RATIO OF RADIANT TO TOTAL HEAT TRANSFERRED THROUGH STEAM LAYER OF WIDTH 0.02CM.

FIGURE II (8)

size reduces the ratio of radiant heat transport to heat conducted across the fluid gap.

Approximate effective mean values of the coefficient of absorption of steam for the temperature and pressure ranges to be covered by this experimental work may be calculated using values quoted in Dorsey (61). The variation of the ratio of radiant to total heat transferred, for the temperature range to be covered by this work, has been calculated by the author for a cell gap size of 0.2 mm and cell surfaces emissivities varying from 0.04 to 1 (see figure II (8)). Almost identical values will be obtained whether the reflections at the cell surfaces are considered diffuse or regular.

It is interesting to see how well the 'transparent' approximation values agree with those found by using the exact approach. Since the optical thickness of the test layer is very small good agreement is expected.

as $\tau \longrightarrow 0$

$$f(\epsilon,\tau) \longrightarrow \frac{3}{4} \cdot \frac{\epsilon}{2-\epsilon} \cdot \tau$$

and $$\bar{q}_r \longrightarrow \frac{16}{3} \cdot \frac{n^2 \sigma T^3 \Delta T}{\tau} \cdot \frac{3}{4} \cdot \frac{\epsilon}{2-\epsilon} \cdot \tau$$

$$= \frac{n^2 \sigma (T_1^4 - T_2^4)}{\frac{2}{\epsilon} - 1} \qquad \text{.... III (M)}$$

which is, of course, the equation for radiant heat transferred across a transparent gas enclosed between two parallel plates at steady state conditions. The values obtained by using the 'transparent' approximation are compared with values found by using the exact approach in figure II (8). For cell surfaces of emissivity of 0.04 use of this approximation would yeild values of thermal conductivity which are some 0.005% high and hence for this gap size the error may be considered negligible.

Summarising it can be stated that for cells in which thermal conductivity determinations are to be made steps should be taken to ensure that the radiative component is very small compared to the conductive component. Even when using the exact approach several simplifying assumptions (see Poltz) such as replacing the absorption coefficient of the test fluid, depending on wavelength, by an effective constant coefficient, have to be made. In general the optical properties of test fluids are not accurately known particularly over large ranges of pressure and temperature. Assessment of the radiative component for fluid layers with very small optical thicknesses by using 'transparent' corrections will show good agreement with those values found by using the exact approach. However, for cells with surfaces of low emissivity (which is the usual case so that the radiative component will be kept small) and test fluids having appropriate absorption, the value of radiant heat transfer may be some 10 times greater than that found by assuming the test medium to be transparent. (see figure II (7)). In these cases not only will assessment of the radiation correction by assuming the test medium transparent cause high values of thermal conductivity to be obtained but results will show, as would be the case if no correction at all were applied, the thermal conductivity of the test medium to depend on cell gap size.

Values of the optical properties of steam at high pressures are not known and can only be roughly estimated. For a range of optical thicknesses of steam layer to be encountered at pressures the deviation of the exact approach values from the 'transparent' correction will increase with increasing optical thickness. If more accurate thermal conductivity values are to be obtained work in measuring the optical properties of steam at high pressures should be undertaken.

II 4 (C) Factors Affecting The Cell Constant
The Change of Cell Dimensions with Temperature

The dimensions of the cell which are measured at 20°C will, of course, change when the cell expands with temperature and allowance for thermal expansion must be made. For the case of silver the equation used is

$$L_t = L_0\left(1 + 19.494 . 10^{-6} t + 1.0379 . 10^{-9} t^2 + 2.375 . 10^{-12} t^3\right)$$

(where L_t is the length at temperature t , L_0 is the length at 0°C and t is the temperature (°C)).

Eccentricity

If the emitter is not exactly centered inside the receiver then according to Carslaw and Jaeger (58) the basic Fourier equation should be replaced by

$$q = \frac{\lambda\, 2\pi L\,(T_1 - T_2)}{\cosh^{-1}\left(\frac{r_1^2 + r_2^2 - e^2}{2 r_2 r_1}\right)} \qquad \text{.... II (L)}$$

(where e = eccentricity).

Care should therefore be taken to ensure that the cell is accurately centered at the beginning of experiments and will remain accurately centered during experimental tests.

CHAPTER III

THE EXPERIMENTAL APPARATUS

III (1) Introduction

The design of a suitable apparatus with which the thermal conductivity of steam may be accurately determined necessitates extreme care and meticulous attention to detail on the part of the experimenter. The difficulties of design increase as the temperature at which measurements are to be made increases. The heat transfer by radiation and the effect of temperature discontinuity assume increasing importance with rising temperature and the apparatus should be designed such that these effects are minimised. The problems in maintaining stable temperature control become more involved at elevated temperatures and the selection of suitable heat and electrical insulating materials is difficult. The materials with which the cell, the cell container and all essential components inside it are made, must be inert to steam and the choice of reliable stable thermocouples for temperature difference measurement is a most important one.

II (2) The Conductivity Cell

A sketch of the conductivity cell used is shown in figure III (1). The cell is of similar design to that used by such experimenters as Venart (1) and Vines (12). Two cells were used. A brass cell was used for preliminary measurements and was not operated at temperatures above 160°C. A silver cell was used for measurements in the range 100°C - 700 °C. The brass and silver cells were of

THERMAL CONDUCTIVITY CELL

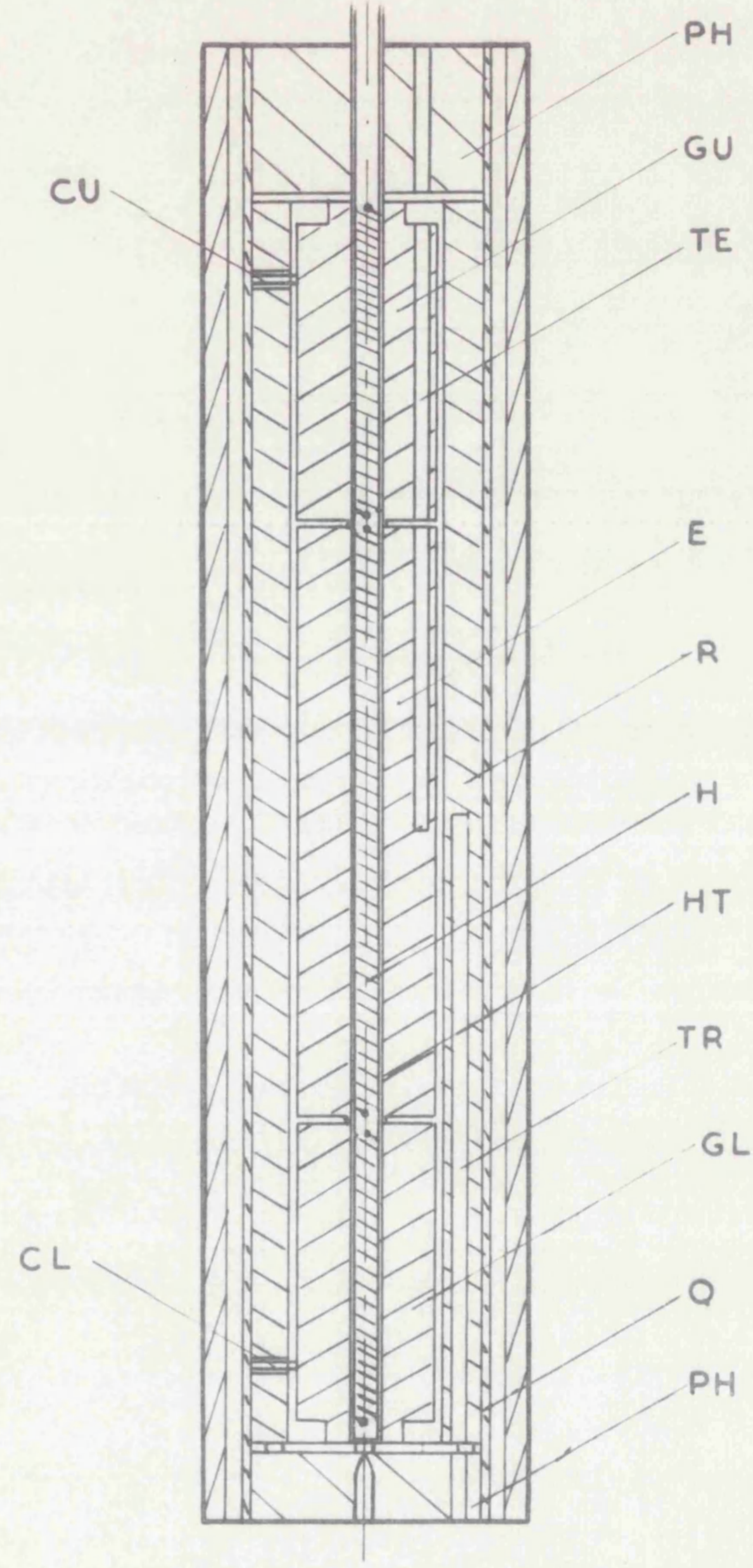


FIGURE III(1)

idertical construction but of slightly different dimensions as shown in table III (1). Only the silver cell will be described.

The cell consists of two cylinders made of pure silver. The inner cylinder is divided into three section, the emitter E and two guard cylinders GU. and GL. In the gaps between the emitter and the guard cylinders additional support is provided by 6 small 1 mm diameter silver pins, 3 spaced at 120° on a 1.5 cm P.C.D. at the top and bottom gaps. The width of the heat guard gaps is 1 mm. Surrounding the inner cylinder is the receiver R. The emitter is located inside the receiver by means of 6 mica spacers 3 spaced uniformly around near the top CU. and 3 similarly spaced near the bottom CL. The spacers are held in position by grub screws.

The complete cell is mounted in a precision bore quartz tube Q. The quartz tube on each side of the cell is filled with accurately machined blocks of carefully fired pyrophyllite PH. A special pre-baking process had to be carried out on these blocks to allow for minimum distortion during firing. This process is outlined by Dyke (62). The thermal constants of pyrophyllite may be taken from the results of experiments carried out by Carte (63).

Silver was chosen as the most suitable cell material because of its inertness to steam and its very low emissivity. It will also be noted, from equation II (G), that the higher the ratio of the conductivity of the test cell material to the conductivity of the test gas the less accurately need the conductivity of the test cell material be known.

The choice of size of gap between emitter and receiver

TABLE III (1)

CELL DIMENSIONS

(a) SILVER CELL

Diameter of emitter	; 0.80445 in	± 0.0001 in
	= 2.0433_{03} cm	± 0.00025 cm
Diameter of receiver	= 0.82033 in	± 0.000024 in
	= 2.0836_{382} cm	± 0.00006 cm
Length of measurement section:	7.50cm	± 0.015 cm
O.D. of receiver	: 3.0 cm	
Surface finish	: 4.10^{-6} in	

(b) BRASS CELL

Diameter of emitter	: 0.75598 in	± 0.0001 in
	= 1.9201_{892} cm	± 0.00025 cm
Diameter of receiver	: 0.78889 in	± 0.00004 in
	= 2.0037_{206} cm	± 0.0001 cm
Length of measurement section:	7.50 cm	± 0.015 cm
O.D. of receiver	: 3.0 cm	
Surface finish	: 4.10^{-6} in.	

ALL MEASUREMENTS MADE AT A TEMPERATURE

OF 20°C.

must be carefully considered. The gap should be made small such that heat transport by convection across the gas gap can be neglected. The gap should also be kept very small such that the ratio of heat transferred by radiation to heat transferred by conduction is small. There are, of course, limitations on how small the gap can be made. The smaller the gap the more accurately both the emitter external diameter and receiver internal diameter have to be machined and finished. Obviously as the gap becomes smaller the uncertainty in the value of the cell constant will be increased. In addition as the gap size is reduced the temperature difference across the steam annulus is decreased for a given heat input to the emitter. Since the thermocouples are located slightly below the cylindrical surfaces of the cell components the temperature drop in the cell material assumes greater importance.

A compromise must therefore be reached. Taking all points into consideration a gap size of 0.2 mm was eventually selected as the most suitable for the objective of these experiments. The final machining of the cell, which had to be machined to within extremely close tolerances was undertaken by the National Engineering Laboratory, East Kilbride, where, with difficulty, it was completed to the tolerances shown in table III (1).

By choosing a gap of this size not only can convection effects be shown to be negligible but, perhaps the most troublesome correction of all, the ratio of heat radiated to heat conducted across the steam, for each temperature at which measurements were made, had a considerably smaller value than that which existed in the cells of previous experimenters who have measured steam in this range. Despite the narrow gap calculations show the temperature drop in the cell material to be very small.

The cell was designed such that the influence of any axial heat flow is very small. This was done in three ways. Firstly, by making the gaps between emitter and guard cylinders of low conductance. Secondly, by the provision of accurate temperature measurement and heater control in the heat guards the temperature of the heat guards could be accurately matched to the temperature at the centre of the emitter. Thirdly, the provision of a powerful heater in the emitter meant that reasonably large radial heat flows could be obtained. In addition, to keep the effects of any end conduction small the ratio of length to diameter ~~ratio~~ of the emitter should be made large. Here again machining to accurate tolerances over a length proves extremely difficult. Typical examples of length to diameter ratio are, for Ziebland and Burton's (40) cell 3.05, for Venart's (1) cell 3.4 and for Vargaftik and Smirnova's (11) cell 3.9. In this cell the ratio is 3.7.

The calculation of heat flow through the centering mechanisms when they are placed in the measurement section can prove difficult. To avoid this difficulty the centering mechanisms in this cell are located well beyond the measuring section of the emitter. Hence the accurate corrections which had to be applied in the case of Keyes and Sandell's (9) and Keyes and Vines (10) cells do not need to be applied in this case. The cell could be accurately centered at 20°C such that eccentricity could not be more than 0.0002" and the effects of possible eccentricity caused by thermal expansion are very small.

COMPONENT DETAILS

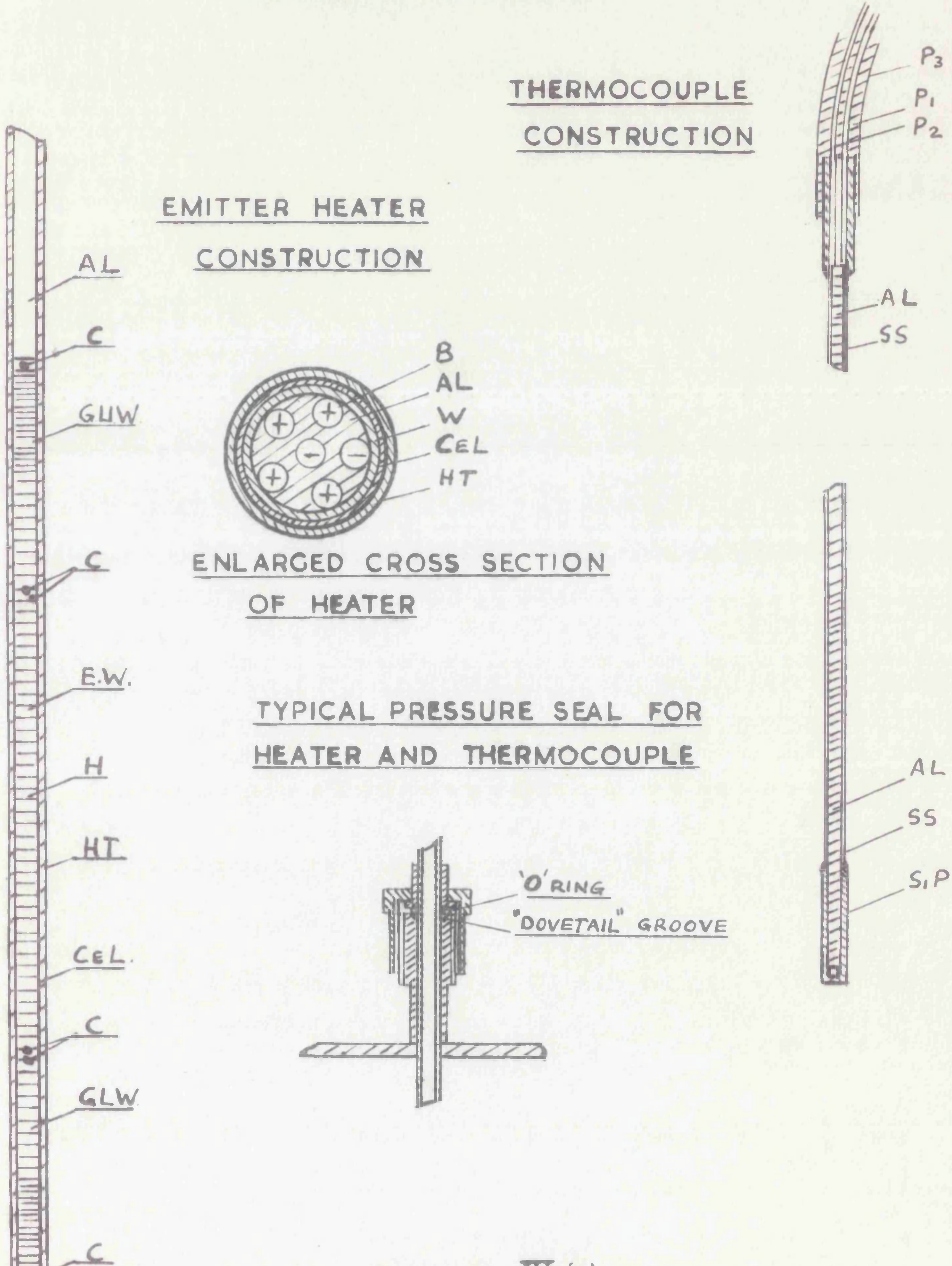


FIGURE III (2)

III (3) The Central Heater

A drawing of the heater is shown in figure III (2). To avoid contamination the heater H is enclosed, a press fit inside the slim stainless steel heater tube HT. of outside diameter some 3.2 mm sealed at one end by means of a stainless steel end plug, silver soldered, with a high temperature solder, to the tube SP. The heater consists of a 6 bore 1.8 mm diameter alūmina insulator AL. bore size 0.4 mm on which the main EW. and guard heater GUW., GLW. windings are wound. The windings are of 41 swg nichrome wire and are cemented in position by a high temperature refractory cement Ce.L. Current carrying copper leads (32 swg) are silver soldered to the ends of the three windings and potential leads (36 swg chromel) are also attached to the ends of the main winding. Small holes, C., were cut in the alumina tube at the end of each winding so that each current and potential lead could be inserted into the appropriate bore. These holes had to be carefully bored by means of a diamond cutter. The leads of the heaters are then carried to the outside of the furnace enclosed in the bores, B., of the central insulator which, in turn, is enclosed in the heater tube. Due to the small diameters of the wires and tubes used this heater proved, at first, difficult to manufacture.

The main advantage of this construction is that with the cell guard heater temperatures matched, as they were in experiments, to the temperature at the centre of the emitter axial heat exchange between individual heater sections is, if not eliminated, reduced to an extremely small value.

The electrical circuit for the heaters is shown in figure III (3). The D.C.supply to the heaters is provided from two 72 volt banks of heavy duty batteries. Any voltage between 2v and 72v can be selected. The power input to the emitter heater is obtained by measurement of the voltage drop across the heater, utilising an accurately calibrated potential divider, and the current flowing through the heater, by measuring the voltage drop across a standard resistor, of accurately known resistance, placed in series with the heater. The power input to the guard heaters is measured using ammeters A_1 and A_2 and voltmeters V_1 and V_2 placed as shown in the guard heater circuits. The supply of power to each of the heaters is controlled by means of rheostats R(H), R(1), R(2). With this circuit the power to the heaters can be accurately controlled and the power input to the emitter heater can be accurately determined. Due to stable battery supply, variations in power over the periods at which steady state readings were taken was slight being of the order of 1 part in 10^3. A special two rate battery charger with both 'quick' and 'trickle' charge rates is provided. The batteries can be readily recharged after use by means of the 'quick' charge. During periods when the batteries are not in use they may be kept fully charged with the specific gravity of the acid at its maximum by the use of the 'trickle' charge.

III (4) The Thermocouples

Careful selection and preparation as well as design of the thermocouples and thermocouple pockets are essential for accurate temperature difference measurement. Sources of error such as heat flow

D.C. ELECTRICAL CIRCUITS

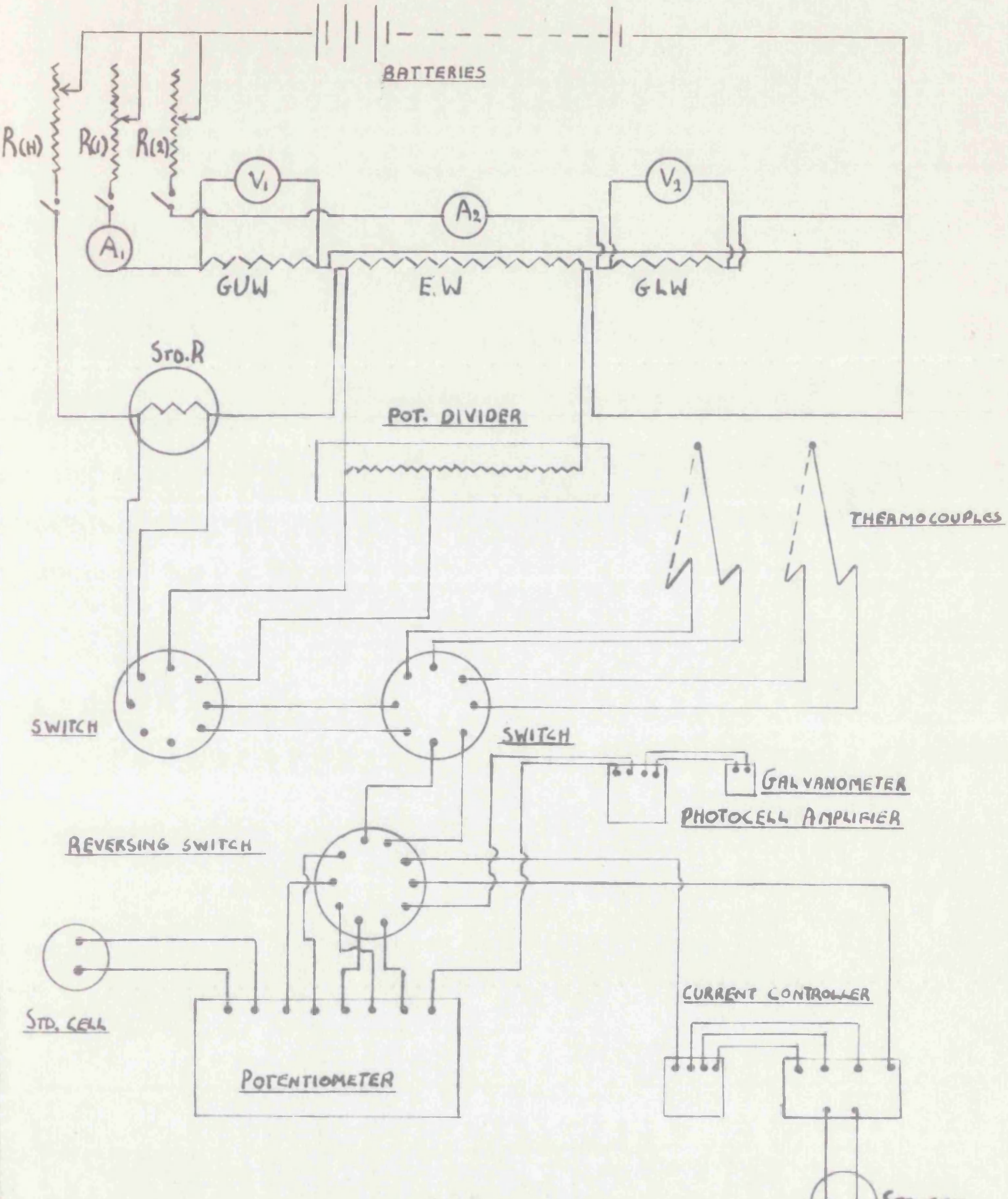


FIGURE III (3)

along the thermocouple wires and tubes near the hot and cold junctions, poor thermal contact at the junctions, straining of the wires, inhomogeneities in the wires, contamination of the wires and poor electrical insulation must be considered. Design should also be such that in the event of a thermocouple proving faulty it can easily be replaced in the cell.

In figure III (1) the thermocouple wells TE. and TR. are shown and are provided to enable measurement of the temperature difference across the steam gap to be made. Thermocouple wells are also provided in the heat guards so that the temperature of the heat guards may be accurately matched to the temperature at the centre of the emitter. The thermocouples, see figure III (2), are made from carefully annealed 33 swg Pt - 13% Rh.Pt. wires. The thermocouple wire was annealed by electrically heating at a temperature of approximately 1400°C for a period of some 30 minutes. During this process the wire was carefully supported over its complete length and the temperature of the wire was measured by means of a radiation pyrometer. Pt-13% Rh.Pt. wires were chosen because of their stability and reliability.

The thermocouples are supported in slim 2 bore 1.2 mm diameter alumina tubes AL. They are then enclosed in thin walled stainless steel tubes SS, of outside diameter 1.5 mm, sealed at one end by means of small silver cylinders SiP. which are silver soldered to the ends of the stainless steel tubes with a high temperature silver solder. The hot junctions press against the silver end plugs which maintain close thermal contact in the thermocouple wells.

The advantage of this construction is that while the hot junctions are in good thermal contact with the cell, due to the silver end plugs, the possibility of heat flow from the junction is considerably reduced by using slim stainless steel tubes. The thermocouples may also be quickly interchanged, as a check, when comparing e.m.f.s

The cold junctions are soft soldered to copper leads which are attached to the potentiometer circuit. The soft soldered junctions are immersed in long glass tubes sealed at one end and filled with moisture free paraffin wax. The glass tubes are immersed in a carefully prepared ice bath which provides zero reference temperature. At all points between where they emerge from the furnace and the ice bath the wires are supported in thick P.V.C. sleeving P_1, P_2, P_3 to prevent undue straining.

The electrical circuit for the thermocouples is shown in figure III (3).

III (5) Electrical Measurement Apparatus

The electrical circuit for the measurement apparatus is shown in figure III (3). The power input to the D.C. heater at the centre of the emitter and the e.m.f.s of the thermocouples must be accurately measured. This is done by using a Diesselhorst pattern thermo-electric free potentiometer which is particularly suitable for the measurment of small e.m.f.s since parasitic thermal e.m.f.s, which are set up when the potentiometer circuit switches are operated, are self eliminating. The potentiometer has two ranges 2×10^{-1} volts and

2×10^{-2} volts. An automatic current controller controls the potentiometer current to 1 part in 10^6. A photocell galvanometer amplifier provides amplification in the detection circuit. The sensitivity is such that, with Pt-13% Rh.Pt thermocouples, temperature discriminations of 2.5×10^{-3} °C can be made. To reduce errors due to switching the switches, which utilise thick copper terminals and spring loaded copper switching leaves, are completely immersed in heavy guage copper tanks filled with moisture free paraffin. When attaching the copper wires in the circuit to the switches care was taken to ensure that good soldered joints were made. So that the effects of thermal e.m.f.s in the measurement circuit could be allowed for a heavy duty thermo-electric free reversing switch to reverse the potentiometer current and measured e.m.f. is also incorporated in the circuit. The standard cells in both the potentiometer and current controller circuits are kept at a constant temperature by insulating them inside an aluminium box. During experiments the cells were checked several times against the standard cell bank in this laboratory. The voltage of the main A/C power supply to the current controller, galvanometer and photocell galvanometer amplifier is reduced by means of 240/12V transformers placed in the circuits.

III (6) The Thermostat

There are two most important considerations which must be taken into account for the construction of a satisfactory thermostat. Firstly the furnace should be designed such that there is an absence of temperature gradients along the length in which the test cell is enclosed. Secondly it is necessary that at each temperature at which experiments are to be made the temperatures of the furnace should remain accurately constant. It is clear that the provision of accurate instrumentation in the apparatus would serve no adequate purpose without a reliable thermostat.

A cross-section of the thermostat assembly is shown in figure III (5). It consists essentially of a high temperature refractory furnace tube FT. on which three separate winding UW., CW., LW. of 21 swg nichrome wire are spaced and cemented in position. The choice of suitable winding material depends on several factors such as the maximum temperature at which the furnace is to be operated, the mechanical properties of the wires in the temperature range of experiments, the atmosphere in which the windings are to operate, the electrical resistance of the wire and its change with temperature and also the current carrying capacity of the wire. When forming the heating elements the maximum surface area loading of the wire and the optimum spacing of the wire must be taken into consideration. These considerations also refer to the choice of suitable wire for the D.C. electrical heater described in section III (2). The nichrome leads to the heaters are guided to the outside of the furnace in alumina tubes. To avoid excessive Joule heating in the leads, so that they may be conveniently connected to the thermostat electrical circuit, the thickness of the leads used is some 3 times that of the furnace elements. The furnace tube FT. is surrounded by a thick layer of finely grained aluminium oxide powder AL. which is contained in a cylindrical copper shell

THERMOSTAT ELECTRICAL CIRCUIT

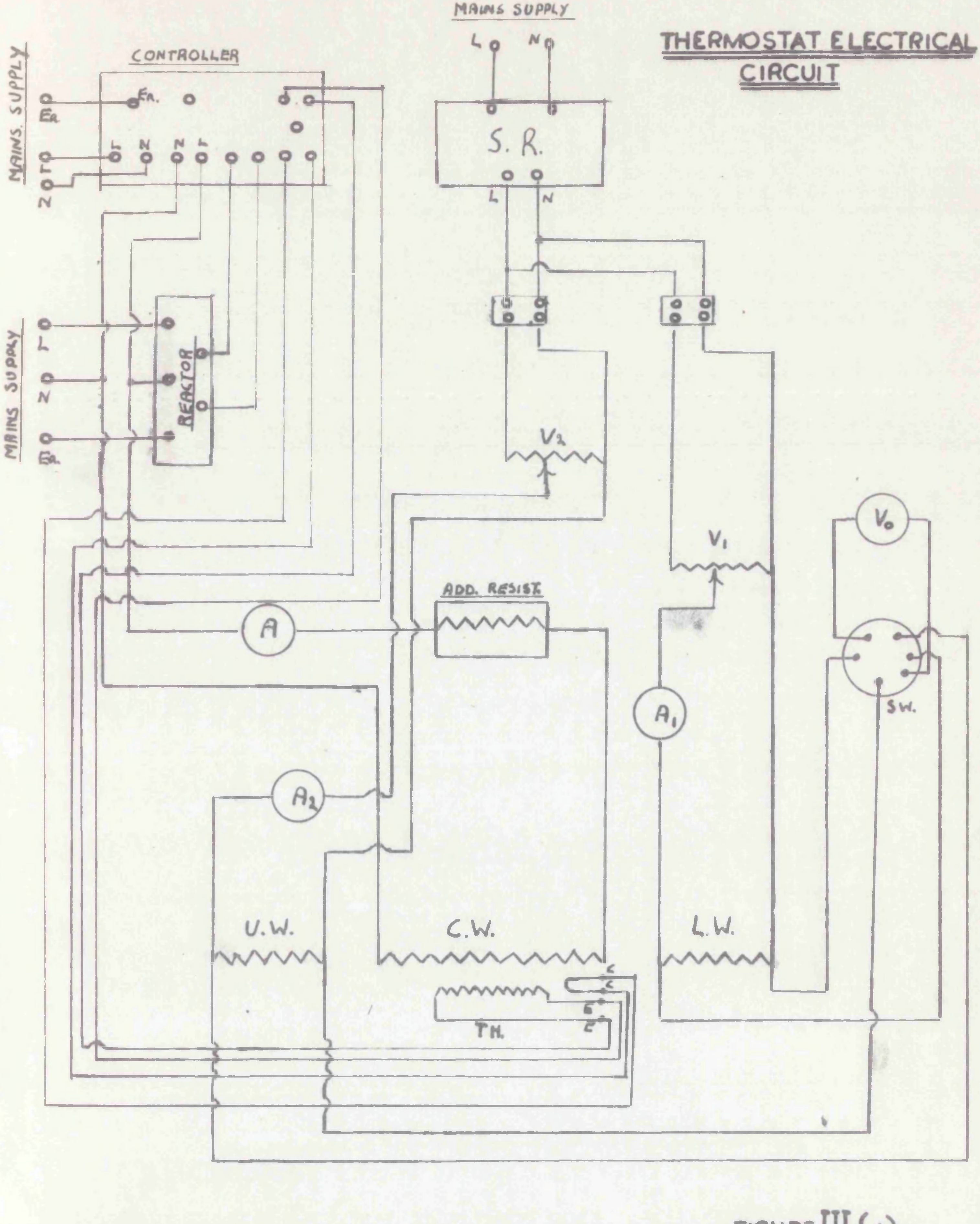


FIGURE III (4)

CS. Obviously the power requirements of the furnace heaters depend largely on the thickness of this insulating layer and the thermal conductivity of the insulating powder (which is dependent on the atmosphere in which it is placed). For particle sizes less than 10^{-2} mm radiant heat transfer between the particles becomes unimportant. While very low conductivity insulations give a quicker thermal response, small changes in the power input to the furnace windings will cause significant temperature changes which will make stable temperature control more difficult. On the other hand, use of higher conductivity insulating materials may lead to excessive power requirements as well as giving slow thermal response. Sindanyo end caps, S., are placed on the ends and the complete assembly is held together and kept rigidly fixed on the test rig framework by means of four steel rods RS. The complete thermostat is placed in a room where the temperature can be controlled to within $\pm$ 0.5°C. The dimensions of the furnace are formulated on the conclusions of Laubitz (64) and the work Motzfeldt (65) was also consulted.

An outline of the electrical circuit for the thermostat is shown in figure III (4). The current to the central winding CW. is controlled by means of a C.N.S., saturable reactor type, proportional temperature controller. The platinum resistance thermometer TH. which affects the control is placed, as shown in figure III (5), next to the central winding. The power input to the central winding can be read from a meter supplied in the controller and the current flowing in the circuit can be measured by means of ammeter A. Manual control of the

THERMOSTAT ASSEMBLY

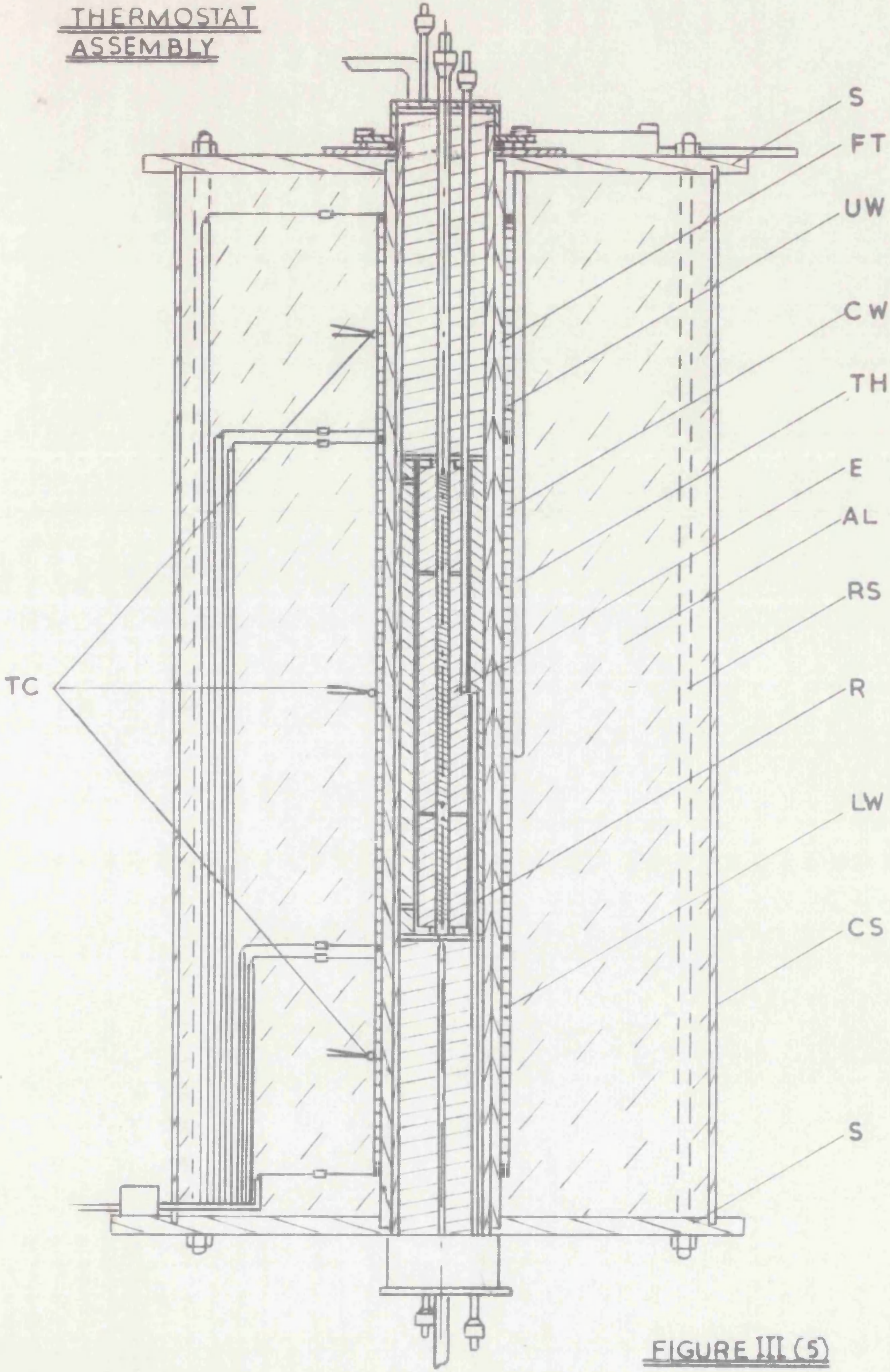


FIGURE III (5)

end heaters UW. and LW. is obtained by means of Variacs V_1 and V_2. The power to the end windings is supplied through a Sorensen Regulator SR. The current flowing through the end windings is measured on ammeters A_1 and A_2 and the voltage across each of the windings is determined by voltmeter Vo. In order to keep a check on the temperature of the windings three quartz insulated chromel-alumel thermocouples TC. (as shown in figure III (5)), are located on the surface at the centre of each winding.

By careful adjustment of the guard heaters the furnace can be controlled such that the gradient along the length of the test cell area can be no more than a few thousandths of a degree. The temperature stability can be controlled such that the variation in temperature over periods of 30 minutes to 1 hour does not exceed $\pm$ 0.02^{o}C and over periods of 5 to 10 minutes is of the order of only a thousandth of a degree.

III (7) The Pressure Equipment

The pressure equipment should be designed such that, by using good seals, no contamination of the steam sample under test occurs. The provision of controlled heaters to keep external portions of the apparatus containing steam at above 100^{o}C allow the steam to be maintained at a pressure close to atmospheric and hence any corrections for 'thermal jump' are kept very small.

The quartz tube containing the cell is sealed at each end by means of stainless steel end caps bearing on Viton 'O' rings

OUTLINE OF EXTERNAL HEATER AND PRESSURE CIRCUITS

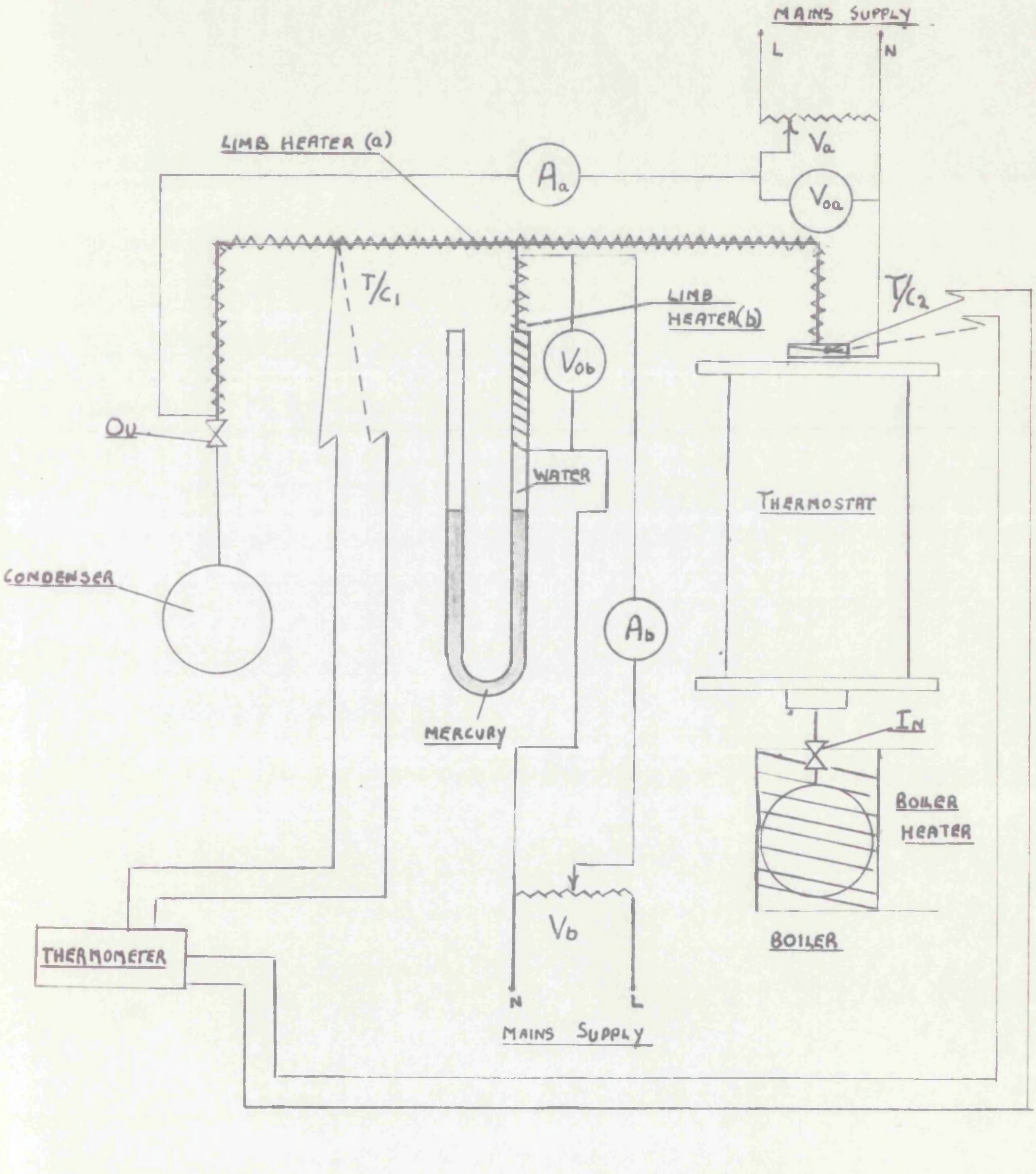


FIGURE III (6)

which are located in "dovetail" grooves at each end of the thermostat, as shown in figure III (5). The thermocouple and heater tubes are sealed in a similar manner, see figure III (2). To ensure good seals the dimensions of the "dovetail" grooves in relation to the diameters of the '0' rings were made as advised by W. Edwards and Co. Ltd. Viton '0' rings were used in preference to ordinary rubber '0' rings since external protions of the apparatus are heated and Viton rings can be used at temperatures above 100°C. Authors such as Yarwood (66) have summarised various types of low pressure seals. Some time was spent in experimenting with ground quartz joints to seal the ends of the apparatus. The excessive care with which these had to be ground together and assembled before a satisfactory seal was produced made them less convenient to use than the metal end caps with '0' ring seals.

A sketch of the pressure circuit is shown in figure III (6). The steam is supplied from the boiler which is filled with pure demineralised water, degassed by boiling. The steam is allowed to pass into the cell via inlet valve IN, and after passing through the circuit is passed to the condenser through outlet valve OU. When a fresh change of steam fills the cell the valves IN and OU are closed. The pressure of the steam is measured by means of a U-tube mercury manometer. The external limbs of the apparatus which contain steam are kept heated at a temperature above 100°C by limb heaters (a) and (b). The heaters are made from quartz insulated nichrome wire and the power to the heaters is controlled by means of Variacs V(a) and V(b). The current taken by each heater is measured on ammeters

A(a) and A(b) and the voltage across each heater is measured on voltmeters Vo(a) and Vo(b). The temperatures along the length of the limbs are measured by 32 swg quartz insulated chromel alumel thermocouples T/c_1 and T/c_2.

CHAPTER 1V

Experimental Procedure and Corrections

1V (1) Experimental Procedure

The cell was assembled in the following manner. The emitter was placed vertically inside the receiver and the 6 mica spacers which were slightly less than 0.2 mm thick were inserted. By careful adjustment of the grub screws which pressed onto the spacers the cell was centered such that a calibrated wire could be passed with equal ease round the gap. Thus eccentricity could not have been any more than 0.0002". The cell was then mounted in the quartz tube and inserted into the test rig. The brass cell used for preliminary measurements was assembled and checked for eccentricity in a similar manner. Due to the difference in gap size a new calibrated wire of appropriate diameter had to be used. In this case eccentricity could not have been more than 0.0002".

The thermostat,which had previously been calibrated,was then switched on. The temperature controller was set to obtain the desired temperature and appropriate adjustments of the guard heaters were made. The cell,which had previously been thoroughly cleaned, was then filled with steam. This was done by allowing steam from the boiler,which had been filled with pure demineralised water, degassed by boiling, to flow through the apparatus for some 2 hours. The gas inlet and outlet valves were then closed AND the the power to the external heaters adjusted so that the pressure of the steam was near atmospheric.

Generally a small pressure of 1-2 cm Hg above atmospheric was maintained so that if any leaks developed in the apparatus they could be readily detected.

When steady state isothermal conditions were reached the e.m.f.s of the thermocouples were intercompared. One of the thermocouples was chosen as the 'standard' thermocouple. In this case the thermocouple which was located in the centre of the emitter was chosen. The e.m.f.s of the other thermocouples were compared with this one and the differences noted. In making measurements of e.m.f. the reversing switch in the circuit was used and readings both 'direct' and 'reverse' were noted. To ensure that the differences were both accurate and consistent the values were checked at intervals over a period of several hours. At each temperature over the range in which thermal conductivity measurements were made this procedure was repeated and plots of the differences against e.m.f. drawn (see appendix (9)). Additional checks were frequently made by quickly interchanging each guard heater thermocouple in turn with the 'standard' thermocouple and again noting if this difference agreed with the original determination. Differences were also noted before and after thermal conductivity determinations were made. It is considered that the error in the differences used to calculate the thermal conductivity did not exceed 0.1 μV.

The D.C. heater in the centre of the emitter was then switched on in order to establish a suitable temperature difference across the steam annulus. In these experiments various temperature differences were used varying between 1 C^{o} and 5 C^{o} but were usually of the order of 2 C^o - 3 C^o. The cell guard heaters were then adjusted so that the temperature difference between the centre of the emitter and the guard heaters did not exceed 0.1 μV. When steady state conditions were reached determinations of the apparent thermal conductivity were begun.

Readings of the thermocouple e.m.f.s,the voltage drop across the emitter heater and the current flowing through the emitter heater were taken at regular intervals over a period of some 20 to 30 minutes. Readings both 'direct' and 'reverse' were noted. Measurements of the current flowing in each of the guard heaters as well as the voltage across each of the guard heaters were also made. This procedure was repeated for all temperatures at which thermal conductivity determinations were made.

Over the intervals of time in which steady state readings were taken the variations in mean temperature did not generally exceed $\pm$ 0.02 C^o and in many cases was less than $\pm$ 0.01 C^o. Over 5 to 10 minute intervals variations were of the order of a few thousandths of a degree. The temperature differences between the thermocouples were constant (small variations of the order of 2.5 x 10^{-2} μV were noted in some cases) and only slight variations of the order of 1 part in 10^3 in the power input to the emitter were noted in these periods. In several cases as an additional check the thermocouples were again interchanged while the apparatus was at steady state conditions and the e.m.f.s intercompared. This always confirmed the accuracy of the original intercomparisons.

The apparatus was frequently charged with a new sample of steam.

So that experience could be gained in operating the apparatus and to confirm that the test rig could be used to obtain accurate thermal conductivity values it was decided that measurements for two gases in the temperature range 100°C - 300°C should first be obtained. Measurements on nitrogen and argon (68) were first completed and the results are presented in a paper at the back of this work along with some preliminary measurements made using the brass cell in the temperature range 140°C - 180°C.

1V (2) Corrections to be applied

The corrections which had to be applied can be split into three groups. Corrections to be applied to (a) the measured heat flow, (b) the temperature differance and (c) the cell constant. Most of these corrections have already been discussed in chapter II. It is the purpose of this section to indicate the magnitude of these corrections when applied to this work. Detailed evaluations of these corrections are given in the appendices.

1V (2) (A) Corrections to the Measured Heat Flow

Consideration of the corrections to be applied for power measurement, radiation, Joule heat generated in the heater leads, convection andaxial heat flow is now given.

Power Measurement Corrections

So that the voltage drop across the emitter heater could be measured on the potentiometer a volt ratio box was used. Since the box was placed in parallel with the heater the measured current which flowed through the standard resistance, which was placed in series with the heater, was slightly greater than the current flowing through the actual heater. Knowing the current flowing through the standard resistor, the resistance, calibration and potential drop across the box, this correction can be made (see appendix (1)). In all cases correction meant that the measured power had to be reduced by approximately 0.5%

Joule Heat in Heater Leads

A small amount of heat was generated in the heater leads in the measurement section of the test cell. This effect was taken into account for each temperature at which measurements were made and in nearly all cases amounted to less than 1% of the total heat input. See Appendix (3).

Convection

In these experiments the Grashof-Prandtl product was very small being approximately 4.9×10^{-4} at 150°C (for the brass cell Gr.Pr $\doteq 3.9 \times 10^{-3}$) which is well below the limit for which laminar convection effects become important.

Axial Heat Flow

The influence of axial heat flow caused by inaccurate matching of the thermocouples was noted at each temperature at which conductivity determinations were made. However, in order to make a more accurate assessment of this influence a series of tests were carried out (see appendix (2)). From these experiments it will be noted that the maximum possible influence of axial heat flow on the thermal conductivity determinations could only have amounted to some 0.7%

Radiation

This correction has been fully discussed in chapter II where it was noted that the assumption that the steam sample was transparent to thermal radiation was allowable for the range of values to be covered by this experimental work, since any error involved by using this assumption is negligible. The magnitude of the correction to be applied at each temperature is shown in appendix (4). It will be seen that the maximum correction which had to be applied, at the highest temperature at which experiments were performed, was only some 0.6% of the total heat input to the emitter heater.

IV (2) (B) Corrections applied to Measured Temperature Difference

Two corrections had to be made to the calculated temperature difference. The effects of the temperature drop in the cell material and the effects of temperature discontinuities at the cell surfaces had to be taken into account.

The Temperature drop in the Cell Material

The magnitude of the temperature drops in the emitter and receiver were calculated as shown in appendix (5). As the thermal conductivity of steam increases with increasing temperature and the thermal conductivity of silver decreases with increasing temperature this effect becomes more important at elevated temperatures. At 600°C it accounts for some 0.5% of the measured temperature difference.

Temperature Discontinuities at the Cell Surfaces

The effects of 'temperature jump' at the cell surfaces were kept very small in experiments by utilising the external heaters provided to keep the steam at a pressure slightly above atmospheric. The values of these effects were calculated as shown in appendix (6). The maximum influence being at 604°C where this effect accounts for some 0.6% of the measured temperature difference.

1V (2) (C) Correction applied to the Cell Constant
The change in Cell Dimensions with Temperature

Corrections had to be applied to take into account the change of cell dimensions with temperature. The change in cell oonstant value was due to the increase in length of the cell with temperature since the differential expansion effect due to the temperature difference between emitter and receiver had negligible effect on the log ratio of the radii of the receiver and emitter which were, of course, of the same material and had the same coefficient of thermal expansion.

Over the complete temperature range the cell constant changed by some 0.97%. For calculation of cell constant see appendix (7).

1V (3) Estimation of Error

The various errors to which measurements were subject are now taken into account. The factors affecting each of the variables used in the basic Fourier equation

$$\lambda = \frac{q \log_e \frac{d_2}{d_1}}{2 \pi L \Delta T} \qquad \text{.... II (E)}$$

such as the accuracy with which the actual measurements were made, the accuracy of the corrections which had to be applied and the accuracy of subsidiary data used, must be considered.

The uncertainty in thermal conductivity, $\delta\lambda$, due to the probable uncertainties in each of the individual variables used, δx, may be expressed as

$$\frac{\delta\lambda}{\lambda} \cdot \% = \left[\frac{\partial\lambda}{\partial q} \cdot \frac{\delta q}{\lambda} + \frac{\partial\lambda}{\partial(\Delta T)} \cdot \frac{\delta(\Delta T)}{\lambda} + \frac{\partial\lambda}{\partial K} \cdot \frac{\delta K}{\lambda} \right] \cdot 100$$

$$= \left[\frac{\delta q}{q} + \frac{\delta(\Delta T)}{\Delta T} + \frac{\delta K}{K} \right] \cdot 100$$

where

$$\frac{\delta K}{K} = \sqrt{\left(\frac{\delta L}{L}\right)^2 + \left(\frac{\delta d_1}{d_1 \log_e \frac{d_2}{d_1}}\right)^2 + \left(\frac{\delta d_2}{d_2 \log_e \frac{d_2}{d_1}}\right)^2}$$

In addition to these uncertainties the uncertainty in thermal conductivity caused by possible eccentricity and the uncertainties in thermal conductivity caused by uncertainties in the absolute temperature and pressure levels must be taken into account.

Individual errors of less than 0.05% were considered negligible.

Consideration of Individual Variables

1V (3) (A) Error in Heat Flow

From appendix (1) it can be seen that the measured heat flow from the emitter measurement section was calculated from

$$q = X v_e \left[\frac{v_i}{R_{STD}} - \frac{X v_e}{R_B} \right]$$

The probable uncertainty in q due to uncertainties in each of the individual variables may be expressed as

$$\frac{\delta q}{q} \cdot \% = \sqrt{\left(\frac{\partial q}{\partial X} \cdot \frac{\delta X}{q}\right)^2 + \left(\frac{\partial q}{\partial v_e} \cdot \frac{\delta v_e}{q}\right)^2 + \left(\frac{\partial q}{\partial v_i} \cdot \frac{\delta v_i}{q}\right)^2 + \left(\frac{\partial q}{\partial R_{STD}} \cdot \frac{\delta R_{STD}}{q}\right)^2 + \left(\frac{\partial q}{\partial R_B} \cdot \frac{\delta R_B}{q}\right)^2} \cdot 100$$

Considering the uncertainties of the e.m.f. of the standard cell as well as the effects of variation of temperature on the standard cell and potentiometer the uncertainty in voltage measurement was estimated to be $\pm 1 \times 10^{-6}$ volts.

Calibration of the volt ratio box showed that the uncertainty in the value of X used amounted to $\pm 2 \times 10^{-2}$. The uncertainty in the value of the standard resistor was $\pm 1 \times 10^{-5}$ ohms and the uncertainty in the measured resistance of the resistance box was $\pm$ 0.1 ohms.

To this uncertainty in actual measurement must be added the uncertainty due to variation in power supply to the heater over the steady state periods in which readings were taken. In addition uncertainties in the heat flow due to uncertainties in the corrections considered for radiation, axial heat flow, convection and Joule heat dissipated in the heater leads must be considered.

From reference to experiment and calculation uncertainties in q, introduced by uncertainties in radiation and axial heat, were estimated to be, for radiation $\pm$ 0.002 watts at the higher temperatures (at low temperatures the error was considered negligible) and for axial heat $\pm$ 0.007 watts. Errors introduced by convection and Joule heat corrections were estimated to be negligible. As stated in this chapter section (1) only slight variations of the order of 1 part in 10^3 were noted in the power input to the emitter heater during steady state periods of measurement.

By summing all the probable uncertainties considered for a heat flow calculated from X = 499.89, $V_{e(MIN)}$ = 0.02 volts, $V_{i(MIN)}$ = 0.002 volts, R_{STD} = 0.01 Ω and R_B = 9997.1 Ω the uncertainty in λ due to the uncertainty in q was estimated to be $\pm$ 0.45% — $\pm$ 0.55% depending on temperature.

1V (3) (B) Error in Temperature Difference

The probable error in measured temperature difference may be estimated to be

$$\frac{\delta \Delta T}{\Delta T} \cdot \% = \sqrt{\left(\frac{\partial(\Delta T)}{\partial(\Delta e)} \cdot \frac{\delta(\Delta e)}{\Delta T}\right)^2 + \left(\frac{\partial(\Delta T)}{\partial(\Delta e_{CAL})} \cdot \frac{\delta(\Delta e_{CAL})}{\Delta T}\right)^2 + \left(\frac{\partial(\Delta T)}{\partial\left(\frac{de}{dT}\right)} \cdot \frac{\delta\left(\frac{de}{dT}\right)}{\Delta T}\right)^2} \cdot 100$$

(where Δe = the measured temperature difference and Δe_{CAL} = the small e.m.f. difference to be taken into account due to the slightly different e.m.f.s of the thermocouples found under isothermal conditions).

Taking into account all the factors which could have influenced the e.m.f. difference measured by the thermocouples such as the stability of e.m.f. and temperature gradients in the hot and cold isothermal regions and also noting that e.m.f. discriminations of $\pm$ 0.025 μV could readily be detected on the galvanometer scale, due to high amplification in the detection circuit, the limits within which Δe and Δe_{CAL} were known may be estimated to be $\pm$ 0.05 μV. The value of $\frac{de}{dT}$ used was derived from the British Standard Institution's Tables B.S. 1826 and the limits within which it was known may be estimated to be $\pm$ 0.01 $\mu V/^oC$.

The uncertainties in ΔT due to uncertainties in the corrections applied for 'thermal jump' and temperature drop in the cell material must also be considered.

At low temperatures the error due to 'thermal jump' is negligible. At high temperatures the error in ΔT due to uncertainty in the corrections applied may be estimated to be $\pm$ 0.002 C^o.

The effect of temperature drop in the cell material was taken into account by using the equation (see chapter II section 4(A) and appendix (5)).

$$\lambda = \frac{q \lambda_{s1} \log_e \frac{d_2}{d_1}}{2\pi L \Delta T \lambda_{s1} - q\left(\log_e \frac{d_0}{d_2} + \log_e \frac{d_1}{d_2}\right)} \qquad \text{.... II (G)}$$

The probable uncertainty in λ due to uncertainties in each of the variables used for this correction may be expressed as

$$\frac{\delta\lambda}{\lambda}\cdot\% = \sqrt{\left(\frac{\partial\lambda}{\partial d_i}\cdot\frac{\delta d_i}{\lambda}\right)^2+\left(\frac{\partial\lambda}{\partial d_o}\cdot\frac{\delta d_o}{\lambda}\right)^2+\left(\frac{\partial\lambda}{\partial\lambda_{s_1}}\cdot\frac{\delta\lambda_{s_1}}{\lambda}\right)^2}\cdot 100$$

where

$$\frac{\partial\lambda}{\partial d_i}\cdot\frac{\delta d_i}{\lambda} = \frac{q}{2\pi L\Delta T\lambda_{s_1} - q\left(\log_e\frac{d_1}{d_i}+\log_e\frac{d_o}{d_2}\right)}\cdot\frac{\delta d_i}{d_i}$$

$$\frac{\partial\lambda}{\partial d_o}\cdot\frac{\delta d_o}{\lambda} = \frac{q}{2\pi L\Delta T\lambda_{s_1} - q\left(\log_e\frac{d_1}{d_i}+\log_e\frac{d_o}{d_2}\right)}\cdot\frac{\delta d_o}{d_o}$$

$$\frac{\partial\lambda}{\partial\lambda_{s_1}}\cdot\frac{\delta\lambda_{s_1}}{\lambda} = \frac{q\left(\log_e\frac{d_1}{d_i}+\log_e\frac{d_o}{d_2}\right)}{2\pi L\Delta T\lambda_{s_1} - q\left(\log_e\frac{d_1}{d_i}+\log_e\frac{d_o}{d_2}\right)}\cdot\frac{\delta\lambda_{s_i}}{\lambda_{s_i}}$$

For estimated maximum uncertainties in d_i and d_o of $\pm$ 0.01 cm and uncertainty in λ_{s_1} $\pm$ 0.2 W/cm°K the uncertainty in λ due to uncertainties in this correction, over the complete temperature range covered, amounted to $<$ 0.05%.

Summing the probable uncertainties considered for Δe = 20 μV, the uncertainty in λ due to uncertainty in ΔT was estimated to be $\pm$ 0.4% — $\pm$ 0.5% depending on temperature.

1V (3) (C) Error in the Cell Constant

As stated before the probable error in cell constant may be estimated to be

$$\frac{\delta K}{K}\cdot\% = \sqrt{\left(\frac{\partial K}{\partial L}\cdot\frac{\delta L}{K}\right)^2 + \left(\frac{\partial K}{\partial d_1}\cdot\frac{\delta d_1}{K}\right)^2 + \left(\frac{\partial K}{\partial d_2}\cdot\frac{\delta d_2}{K}\right)^2}\cdot 100$$

$$= \sqrt{\left(\frac{\delta L}{L}\right)^2 + \left(\frac{\delta d_1}{d_1 \log_e \frac{d_2}{d_1}}\right)^2 + \left(\frac{\delta d_2}{d_2 \log_e \frac{d_2}{d_1}}\right)^2}\cdot 100$$

As shown in Table III (1)the maximum uncertainties in d_1, d_2 and L were $\pm$ 0.0001", $\pm$ 0.000024" and $\pm$ 0.015 cm. The tolerance of $\pm$ 0.0001" for the diameter of the emitter was somewhat higher than that requested by the author but due to difficulties in machining, a better tolerance could not be obtained.

The error in cell constant due to uncertainties in the correction applied for thermal expansion was estimated to be negligible.

For the uncertainties considered the uncertainty in λ due to uncertainty in the cell constant may be estimated to be $\pm$ 0.67%.

1V (3) (D) <u>Error Due to Eccentricity</u>

From Chapter III section 4 (C) it will be noted that if the emitter is not exactly centered inside the receiver the basic Fourier equation should be replaced by

$$\lambda = \frac{q \cosh^{-1}\left(\frac{r_1^2 + r_2^2 - e^2}{2 r_1 r_2}\right)}{2\pi L\ (T_1 - T_2)} \quad \dots \text{II (L)}$$

At 20°C a check for eccentricity showed that it could not be more than 0.0005 cm. (See chapter 1V section (1)). Due to thermal expansion of the cell this eccentricity could, under the worst possible conditions, be shown to increase to 0.00075 cm.

'Probable' eccentricity may be estimated to cause an error in λ of some 4 parts in 10^4 for this cell.

1V (3) (E) Errors due to Absolute Pressure and Temperature Level Uncertainties

Any error in thermal conductivity due to error in absolute pressure measurement was estimated to be negligible.

From calibration of the thermocouples the maximum error in absolute temperature measurement was estimated to be $\pm$ 0.3%. The sensitivity of temperature measurement was of a higher order of accuracy being $\pm$ 0.01 $^{\circ}$C. This uncertainty introduced uncertainties in λ of 0.15% - 0.3% depending on temperature.

1V (3) (F) Overall Estimation of Error

Summation of all the errors shows that the probable accuracy of the results obtained in these experiments can be estimated to be within $\pm$ 1.5% - $\pm$ 2%, depending on temperature.

The expected level of precision in these measurements is estimated to be $\leqslant \pm$ 1% over the complete temperature range.

1V (3) (G) Estimation of Error for Preliminary Measurements

Similar estimation of error for the brass cell shows that the uncertainties in λ due to uncertainties in the heat flow, the temperature difference and the cell constant may be estimated to be

$\pm$ 0.45%, $\pm$ 0.41% and $\pm$ 0.4% respectively. Any error due to eccentricity would change the cell oonstant by less than 1 part in 10^5 and uncertainty in λ due to uncertainty in absolute temperature may be estimated to be $\pm$ 0.1%.

Summation of all the errors will show that probable accuracy of the results obtained with the brass cell can be estimated to be within $\pm$ 1.5% .

The expected level of precision for these preliminary measurements is estimated to be $\leqslant \pm$ 1%.

CHAPTER V

RESULTS

V (1) Introduction

The experimental determinations of the thermal conductivity of steam at atmospheric pressure found in this work are now presented in tables V (3) and V (4). The results were obtained in four main series of tests. The first series of measurements were carried out using the brass cell in the temperature range 140°C - 150°C. Three main series of tests were carried out using the silver cell at temperatures up to 603°C. Since the values obtained between 150°C and 250°C, while in very good agreement with the correlated values of the National Bureau of Standards (18) and Vargaftik and Zimina (14), suggested slightly lower values than those given in these correlations additional measurements were carried out in this range to confirm the accuracy of the original determinations. Each of the values quoted in the tables is the result of some 5 to 7 determinations. Figure V (1) shows the variation of thermal conductivity with temperature found in this work and typical examples of steady state test runs for the brass and silver cells are given in tables V (1) and V (2) respectively.

V (2) Specimen Calculations

The following calculations are typical of how each value of thermal conductivity was evaluated from the data obtained in experiments.

V (2) (A) Preliminary Measurements (Brass Cell)

From equation II (E) thermal conductivity may be evaluated from

$$\lambda'_{APPARENT}' = \frac{\log_e \frac{r_2}{r_1}}{2\pi L} \cdot \frac{q}{\Delta T}$$

which may be written as

$$\lambda'_{APPARENT}' = \frac{\log_e \frac{r_2}{r_1}}{2\pi L_o(1+20\cdot 3.10^{-6}T)} \cdot \frac{\frac{X\, v_e\, v_i}{R_{STD}}}{\frac{\Delta e}{\frac{de}{dT}}} \quad \text{.... V (A)}$$

(See appendices (1) and (7)).

The following calculation is for the test run values given in Table V (1) where

e mean = 985.09 μV

$\therefore$ T mean = 143.8°C (From reference to thermocouple calibration. See apendix (9)).

Δe = 26.5 μV (See appendix (9)).

$\frac{de}{dT}$ = 8.12_7 μV/°C (Computed interpolated value obtained from reference to B.S. 1826 tables).

$i_{L.G.H.}$ = 200 mA (where i_{LGH} = current which flowed in lower guard heater during steady state run. See appendix (3)).

v_e = 0.01493_5 V

v_i = 0.001380 V

In this case corrections must be made for current flow in the volt ratio box, Joule heat in the heater leads, radiation and temperature drop in the cell material. The methods by which these corrections are calculated are given in appendices (1), (3), (4) and (5). Taking into account these corrections equation V(A) becomes

$$\lambda = \frac{\log_e \frac{r_2}{r_1}}{2\pi L_0 (1+20.3 \cdot 10^{-6} T)} \left[\frac{X v_e \left(\frac{v_i}{R_{STD}} - \frac{X v_e}{R_B} \right) + \left(\Sigma i^2 R_T \right) - \frac{\sigma 2\pi r_1 L (T_1^4 - T_2^4)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)}}{\frac{\Delta e}{\frac{de}{dT}} - \frac{q}{2\pi L \lambda_b} \left(\log_e \frac{r_1}{r_i} + \log_e \frac{r_a}{r_2} \right)} \right]$$

(Symbols used are as defined in appendices (1), (3), (4), (5) and (7)).

Inserting the appropriate values

$$= \frac{(\log_e 1.04353_3) \left[(499.89)(0.01493_5) \left\{ \frac{0.001380}{0.01} - \frac{(499.89)(0.01493_5)}{9997.1} \right\} \right.}{(6.28318)(7.497_0)(1+(20.3)(10^{-6})(143.8)) \left\{ \frac{26.50}{8.12_7} - 0.00946 \right\}} \text{ cont'd}$$

$$\left. + 0.00493 - 0.0044 \right]$$

$$= 28.45 \times 10^{-5} \ {}^{W}/_{cm\ {}^{o}K}$$

V (2) (B) Silver Cell Measurements

From equation II (E) the thermal conductivity may be calculated. This equation may be written as

$$\lambda_{\text{'apparent'}} = \frac{\left(\log_e \frac{r_2}{r_1}\right) \frac{X\, V_e V_i}{R_{STD}}}{2\,\pi L_o \,(1{+}19.494\text{x}10^{-6}T \quad {+}1.0379\text{x}10^{-9}T^2 \quad {+}2.375\text{x}10^{-12}T^3)\,\frac{\Delta e}{\frac{de}{dT}}} \quad \text{.... V (B)}$$

(see appendices (1) and (7)).

The following calculation is for the test run shown in table V(2).

e_{mean} = 1515.1_3 µV

T_{mean} = 205.9°C (From reference to thermocouple calibration. (see appendix (9)).

Δe = 21.7_{75} µV (see appendix (9)).

$\frac{de}{dT}$ = 8.88_4 µV/C° (Computed interpolated value from reference to B.S.1826 tables)

i_{LGH} = 280mA (where i_{LGH} = current which flowed in lower guard heater during steady state run. See appendix (3)).

V_e = 0.02078 V

V_i = 0.001869 V

For T_{mean} = 205.9°C equation becomes

$$\lambda_{\text{'apparent'}} = \frac{\left(\log_e \frac{r_2}{r_1}\right) \frac{X\, V_e V_i}{R_{STD}}}{2\,\pi(7.497_1)\,(1.00408)\,\frac{\Delta e}{\frac{de}{dT}}}$$

In this case corrections have to be applied for current flow in the volt ratio box, Joule heat in the heater leads, radiation and temperature drop in the cell material. The methods by which these corrections are calculated are given in appendices (1), (3), (4), and (5). Taking into account those corrections equation V (B) becomes

$$\lambda = \frac{\log_e \frac{r_2}{r_1}}{2\pi(7.497_1)(1.00408)} \left[\frac{\chi v_c\left(\frac{v_c}{R_{STD}} - \frac{\chi v_c}{R_B}\right) + \left(\Sigma i^2 R_T\right) - \frac{\sigma 2\pi r_1 L\left(T_1^4 - T_2^4\right)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)}}{\frac{\Delta e}{\frac{de}{dT}} - \frac{q}{2\pi L \lambda_{s_1}}\left(\log_e \frac{r_L}{r_i} + \log_e \frac{r_o}{r_2}\right)} \right]$$

(Symbols used are as defined in appendices (1), (3), (4), (5), and (7)).

Inserting appropriate values

$$= \frac{\log_e 1.01974_0}{(6.28318)(7.497_1)(1.00408)} \left[\frac{(499.89)(0.02078)\left(\frac{0.001869}{0.01}\right) - \left(\frac{(499.89)(0.02078)}{9997.1}\right) \quad \text{cont'd} \quad + (0.0116) - (0.0028)}{\frac{21.7_{75}}{8.88_4} - 0.00551} \right]$$

$$= 32.78 \times 10^{-5} \left({}^{w}/_{cm\ ^{o}K} \right)$$

V (3) Correlation of Data

The data was fitted by means of least squares analysis to equations of the form favoured by Vargaftik (14).

$$\lambda_1 = a + bt + ct^2 \quad \ldots\ldots\ldots\ldots\ldots$$

(where λ_1 = thermal conductivity at P = 1 atmosphere, t = temperature ($^\circ$C) and a, b and c are constants).

Equations with less than four coefficients did not give very good fits to the data. It was noted that an equation with five coefficients fitted the data slightly better than an equation with only four (see figure V (2)). The addition of a sixth coefficient did not serve to significantly reduce the standard deviation of the experimental points from the equation values.

The equation used to give the equation values given in tables V (3), V (4) and V (5) was

$$\lambda_1 .10^5 = a + bt + ct^2 + dt^3 + et^4 \quad \ldots . \text{ V (C)}$$

Units of λ_1 are $^{W}/_{cm\,^\circ K}$

a = $3.01610331 \quad .10^{+1}$

b = $-1.09490576 \quad .10^{-1}$

c = $8.34091311 \quad .10^{-4}$

d = $-1.31016826 \quad .10^{-6}$

e = $7.67812044 \quad .10^{-10}$

TABLE V (1)

Preliminary Measurements (Brass Cell)

Typical Example of Steady State Test Run

$T_M = 143.8^{\circ}C$

Potentiometer Measurements

Time (Mins)	e mean (μv)	Δe_G (μv)	Δe (μv)	V_e(v)	V_i(v)
Start	984.9_5	+0.025	26.5_0	0.01493_5	0.001380
5	984.9_5	+0.025	26.5_0	0.01493_5	0.001380
10	984.9_5	+0.025	26.5_0	0.01493_5	0.001380
15	984.9_5	+0.025	26.5_0	0.01493_5	0.001380
20	985.1_5	0	26.5_0	0.01493_5	0.001380
25	985.2_5	0	26.5_0	0.01493_5	0.001380
30	985.2_5	+0.025	26.5_0	0.01493_5	0.001380
Rev.	985.2_5	+0.025	26.5_0	0.01493_5	0.001380
End.					
Mean Values	985.0_9	+0.019	26.50	0.01493_5	0.001380

Δe = e.m.f. difference between emitter and receiver

Δe_G = e.m.f. difference between centre of emitter and heat guards

e mean = mean e.m.f. at which measurements were made

V_e = measured voltage drop across heater

V_i = measured voltage drop across standard resistor

(e.m.f. and difference measurements refer to values corrected to take into account the slight differences noted on isothermal intercomparison).

TABLE V (2)

Silver Cell Measurements

Typical Example of Steady State Test Run

$T_M = 205.9^{\circ}C$

Potentiometer Measurements

Time (Mins)	e mean (μv)	Δe_G (μv)	Δe (μv)	V_e(v)	V_i(v)
Start	1515.2_1	0	21.7_5	0.02078	0.001869
5	1515.2_1	0	21.7_5	0.02078	0.001869
10	1515.2_1	0	21.7_5	0.02078	0.001869
15	1515.3_1	0	21.7_5	0.02078	0.001869
20	1515.3_0	0	21.8_0	0.02078	0.001869
25	1515.3_0	0	21.8_0	0.02078	0.001869
30	1515.1_0	0	21.8_0	0.02078	0.001869
Rev.	1514.9	0	21.8_0	0.02078	0.001869
End.					
Mean Values	1515.1_3	0	21.7_{75}	0.02078	0.001869

where Δe = e.m.f. difference between emitter and receiver

Δe_G = e.m.f. difference between centre of emitter and heat guards

e mean = mean e.m.f. at which measurements were made

V_e = measured voltage drop across the heater

V_i = measured voltage drop across the standard resistor

(e.m.f. and difference measurements refer to values corrected to take into account the slight differences noted on isothermal inter-comparison).

TABLE V (3)

Preliminary Measurements (Brass Cell)

Point No.	Temperature (^{o}C)	(λ) observed ($W/M^{o}K$)	(λ_1) equation ($W/M^{o}K$)	Deviation	% Deviation
(1)	142.4	0.0278	0.0280	-0.0002	-0.71
(2)	143.8	0.0285	0.0281	+0.0004	+1.42
(3)	158.6	0.0293	0.0290	+0.0003	+1.03

TABLE V (4)

Silver Cell Measurements

Point No.	Temperature (^{o}C)	(λ_1)observed (W/M^{o}K)	(λ_1)equation (W/M^{o}K)	Deviation	%Deviation
(4)	170.3	0.0296	0.0299	-0.0003	-1.00
(5)	170.6	0.0296	0.0299	-0.0003	-1.00
(6)	171.4	0.0302	0.0300	+0.0002	+0.67
(7)	171.6	0.0299	0.0300	-0.0001	-0.33
(8)	172.8	0.0298	0.0301	-0.0003	-1.00
(9)	205.9	0.0328	0.0329	-0.0001	-0.30
(10)	206.2	0.0327	0.0330	-0.0003	-0.91
(11)	207.2	0.0331	0.0330	+0.0001	+0.30
(12)	207.4	0.0331	0.0331	0	0
(13)	246.4	0.0374	0.0371	+0.0003	+0.81
(14)	246.6	0.0377	0.0371	+0.0006	+1.62
(15)	246.9	0.0374	0.0371	+0.0003	+0.81
(16)	246.9	0.0368	0.0371	-0.0003	-0.81
(17)	247.6	0.0370	0.0372	-0.0002	-0.54
(18)	247.7	0.0371	0.0372	-0.0001	-0.27
(19)	276.4	0.0411	0.0404	+0.0007	+1.73
(20)	276.7	0.0410	0.0405	+0.0005	+1.23
(21)	278.0	0.0404	0.0406	-0.0002	-0.49
(22)	278.0	0.0408	0.0406	+0.0002	+0.49

TABLE V (4) (contd)

Point No.	Temperature (^{o}C)	(λ_1)observed ($W/M^{o}K$)	(λ_1)equation ($W/M^{o}K$)	Deviation	%Deviation
(23)	328.8	0.0463	0.0467	-0.0004	-0.86
(24)	328.8	0.0459	0.0467	-0.0008	-1.71
(25)	328.9	0.0456	0.0467	-0.0011	-2.36
(26)	329.0	0.0465	0.0468	-0.0003	-0.64
(27)	387.9	0.0544	0.0541	+0.0003	+0.55
(28)	387.9	0.0545	0.0541	+0.0004	+0.74
(29)	388.1	0.0545	0.0541	+0.0004	+0.74
(30)	388.3	0.0549	0.0542	+0.0007	+1.29
(31)	467.8	0.0638	0.0641	+0.0003	-0.47
(32)	467.8	0.0641	0.0641	0	0
(33)	467.8	0.0640	0.0641	-0.0001	-0.16
(34)	603.3	0.0816	0.0817	-0.0001	-0.12
(35)	603.3	0.0815	0.0817	-0.0002	-0.24
(36)	603.5	0.0821	0.0817	+0.0004	+0.49

STANDARD DEVIATION: 0.96%

TABLE V (5)

Values given by Correlating Equation V (C)

T (^{o}C)	λ_1 (W/M^{o}K)
150	0.0285
200	0.0324
250	0.0374
300	0.0432
350	0.0494
400	0.0556
450	0.0619
500	0.0682
550	0.0745
600	0.0813
650	0.0887

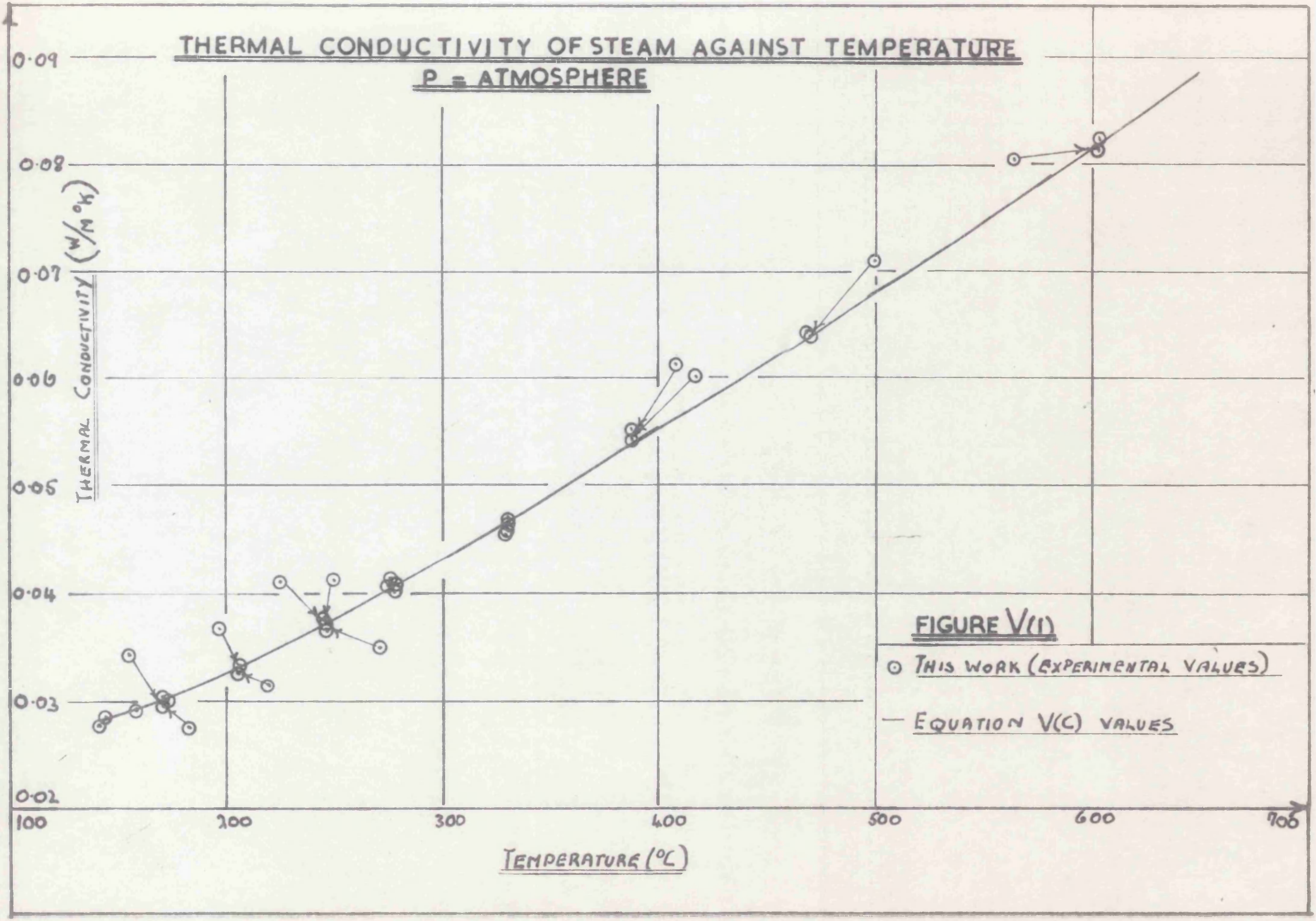
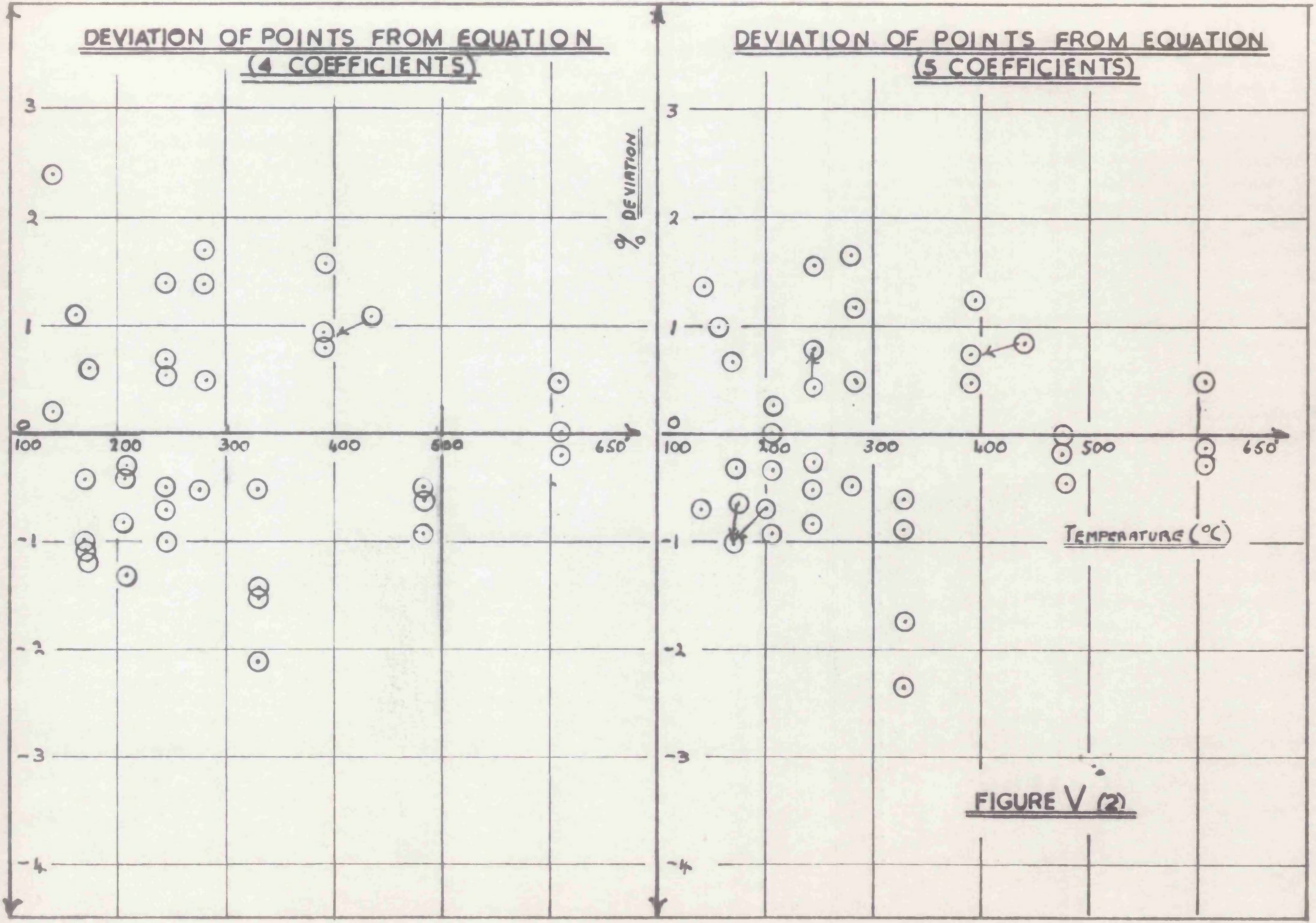

THERMAL CONDUCTIVITY OF STEAM AGAINST TEMPERATURE
P = ATMOSPHERE
THERMAL CONDUCTIVITY (W/M °K)
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
100
200
300
400
500
600
700
TEMPERATURE (°C)
⊙ THIS WORK (EXPERIMENTAL VALUES)
— EQUATION V(C) VALUES

FIGURE V(1)



DEVIATION OF POINTS FROM EQUATION (4 COEFFICIENTS)
DEVIATION OF POINTS FROM EQUATION (5 COEFFICIENTS)
% DEVIATION
TEMPERATURE (°C)
3
2
1
0
-1
-2
-3
-4
100
200
300
400
500
650°

FIGURE V (2)

CHAPTER VI

Discussion, Correlation and Conclusions

VI (1) Discussion

From figures VI (1) and VI (2) it can clearly be seen that the values obtained in this work agree well with the data of Vargaftik and Zimina (14) published in 1963. Severe disagreement with the trend shown by the values above 300 ^{o}C of the correlation of the National Bureau of Standards (18) published in 1966 can also be noted.

The arguments in favour of the lower and higher atmosphere lines have already been discussed in Chapter I but in view of the results found in this experimental work it was thought worthwhile that the main arguments which have been put forward in favour of the lower line should be considered in more detail. The case for lower values rests on the data of Geier and Schafer (13) and the work of Vines (12). It has also been shown by Keyes (10) (see Chapter I section (3)) that on plotting $\frac{T^{\frac{1}{2}}}{\lambda \times 10^{6}}$ against $\frac{\tau \times 10^{3}}{10^{12\tau}}$ for equation I (C) the resulting line obtained intersects the x-axis to the right of the zero point of the axis system. Since this requires that $\lambda = \infty$ at a finite temperature, if an equation of the type favoured by Keyes is used to fit the data, it is suggested that the Russian high temperature values are excessively large.

Firstly let us consider the latter point. Examination of the data used by Keyes shows that, along with other works, the values published by Vargaftik (8) in 1948 were used to substantiate his argument. From figure I(3) it can be noted that all the Russian

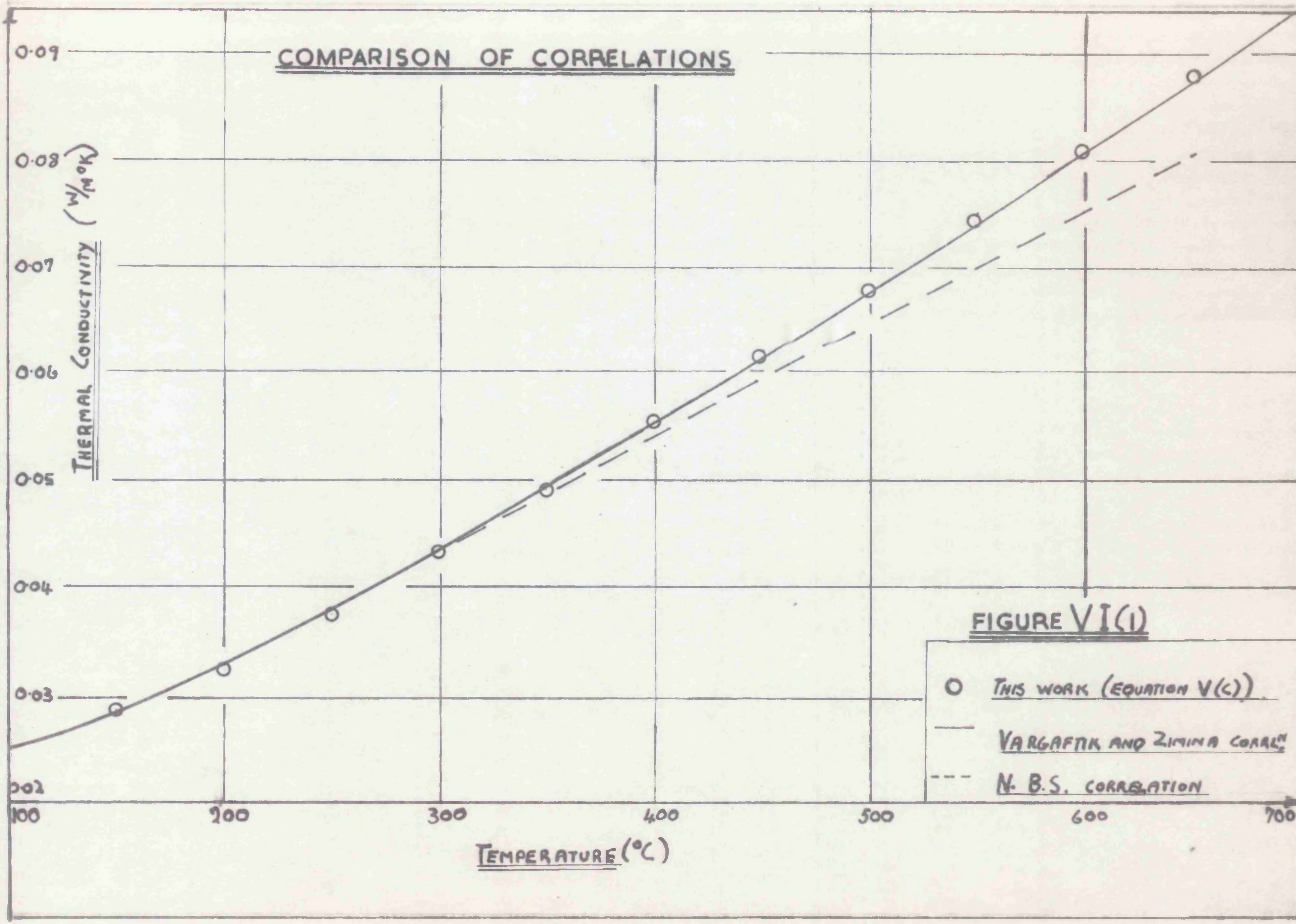

COMPARISON OF CORRELATIONS
THERMAL CONDUCTIVITY (W/M°K)
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
100
200
300
400
500
600
700
TEMPERATURE (°C)
THIS WORK (EQUATION V(c))
VARGAFTIK AND ZIMINA CORRL^{N}
N. B.S. CORRELATION

FIGURE VI(1)

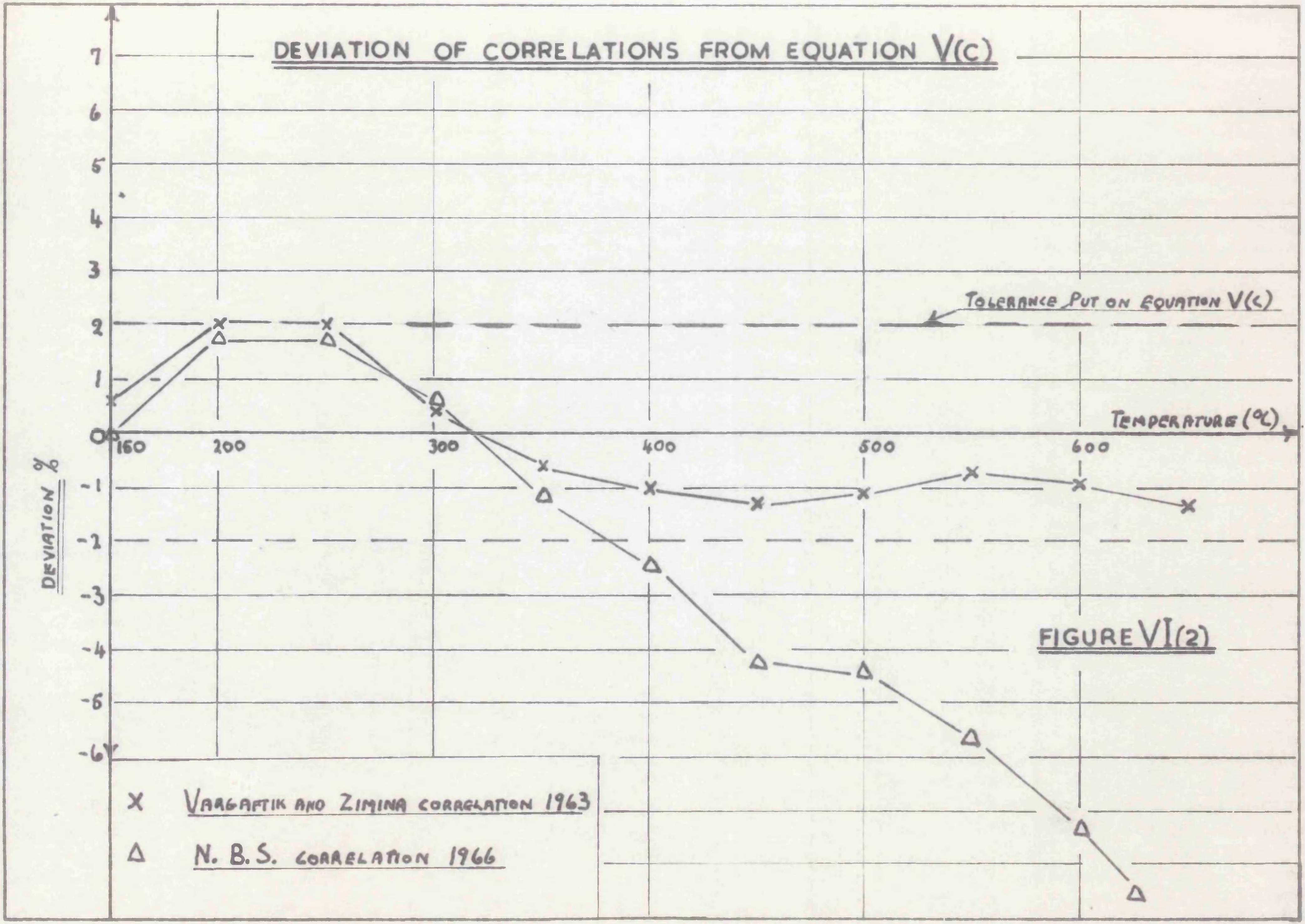
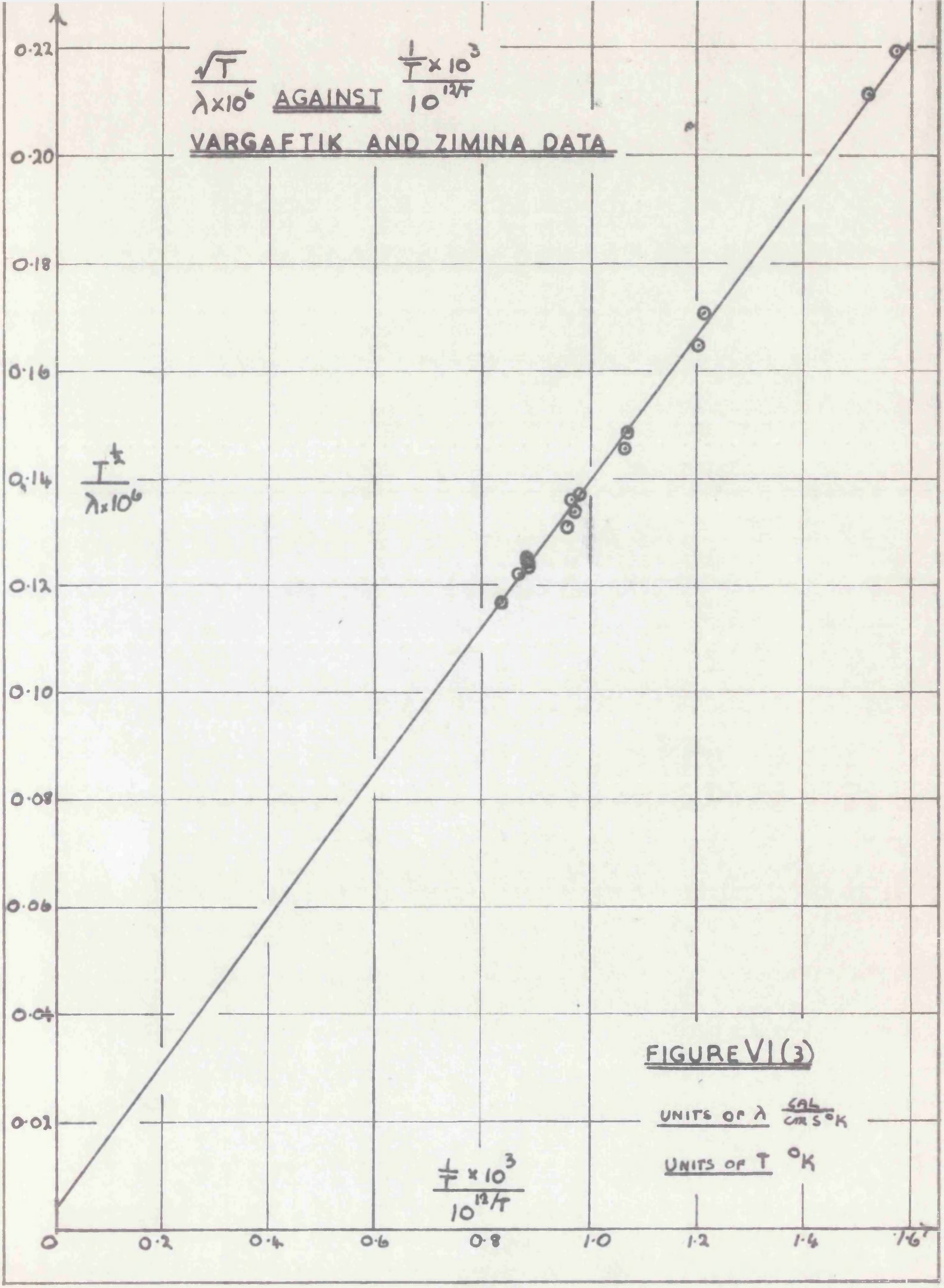

DEVIATION OF CORRELATIONS FROM EQUATION V(C)
TOLERANCE PUT ON EQUATION V(C)
TEMPERATURE (°C)
DEVIATION %
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
160
200
300
400
500
600
X VARGAFTIK AND ZIMINA CORRELATION 1963
Δ N. B. S. CORRELATION 1966

FIGURE VI(2)

data apart from the values published by Vargaftik in 1948, which are several percent higher, show agreement with the most recent experimental data of Vargaftik and Zimina (14) on which the correlating equation I(D), accepted by the Sixth International Conference on the Properties of Steam 1964, is based. It would, therefore, appear essential that the accuracy of Vargaftik's 1948 values be questioned. In addition Vargaftik has stated, some five years ago, that the high temperature data which he published in 1948 was in error and should not be used in any correlation of data. In figure VI (3) $\frac{T^{\frac{1}{2}}}{\lambda \times 10^6}$ against $\frac{\tau \times 10^3}{10^{12\tau}}$ is plotted for the experimental data of Vargaftik and Zimina. It can be seen that intersection of the x-axis to the right of the zero point of the axis system does not take place. From this it is obvious that for this data the argument of Keyes is not valid. In the correlation of data carried out in section (2) of this chapter it will be noted that an equation of the type favoured by Keyes gives a good fit to the data. On plotting $\frac{T^{\frac{1}{2}}}{\lambda \times 10^6}$ against $\frac{\tau \times 10^3}{10^{12\tau}}$ intersection of the line obtained with the x-axis to the right of the zero point of the axis system does not take place.

In order to obtain more information concerning the work of Geier and Schafer, Dr. Bruges (see reference (22)), then acting as coordinator to the Thermal Conductivity Panel of the Sixth International Conference on the Properties of Steam, went to Munich in 1964 to meet Dr. Geier. From the information received it was noted that the measurements of Geier and Schafer on steam had been performed at only one pressure, some 15 cm Hg. Although corrections had been applied to take into account the influence of 'thermal jump' for the other gases which they measured, corrections were not



$\frac{\sqrt{T}}{\lambda \times 10^6}$ AGAINST $\frac{\frac{1}{T} \times 10^3}{10^{12/T}}$
VARGAFTIK AND ZIMINA DATA
$\frac{T^{\frac{1}{2}}}{\lambda \times 10^6}$
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
$\frac{\frac{1}{T} \times 10^3}{10^{12/T}}$
UNITS OF λ $\frac{CAL}{CM\ S\ ^\circ K}$
UNITS OF T $^\circ K$

FIGURE VI (3)

made for steam. Since the internal diameter of the quartz tube used in their test cell was not given, or readily available, it seemed, as is stated by Vargaftik and Zimina (14), that appropriate corrections could not be applied. However, from the information supplied to him by Dr. Bruges the author noted that the approximate dimensions of Geier and Schafer's cell could be determined. It should be stressed here that these calculations are only approximate but serve to give a reasonable indication of how much Geier and Schafer's values would be influenced by applying these corrections. Utilising the modified Stefan-Boltzman equation used by Geier and Schafer to make radiation corrections, the values of the radiative components given by them in their paper and the relationship between heat radiated to the heat transmitted across the steam sample, the ratio $\log_e {}^{r}2/r_1$ (where r_2 = internal radius of the receiver and r_1 = radius of the wire) was estimated. Comparing the estimated value of $2r_1 \log_e {}^{r}2/r_1$ for Geier and Schafer's cell with the value for Vargaftik and Zimina's cell it was noted that the values of the corrections to be applied for 'thermal jump' were similar. From the information given by Vargaftik and Zimina (14) corrections to the values of Geier and Schafer can be made up to a temperature of 750 °C. Calculations show that at 500 °C Geier and Schafer's value should be increased by some 0.6%, at 600 °C by 2.4% and at 700 °C by 3.7%. In figure VI (4) the values obtained by Geier and Schafer (13) and Vines (12) for three gases are compared with recent correlations. For nitrogen they are compared with the correlation of Vargaftik and Zimina (21) and for carbon dioxide and air with correlations carried out at the Thermophysical Properties Research Centre (67). From these

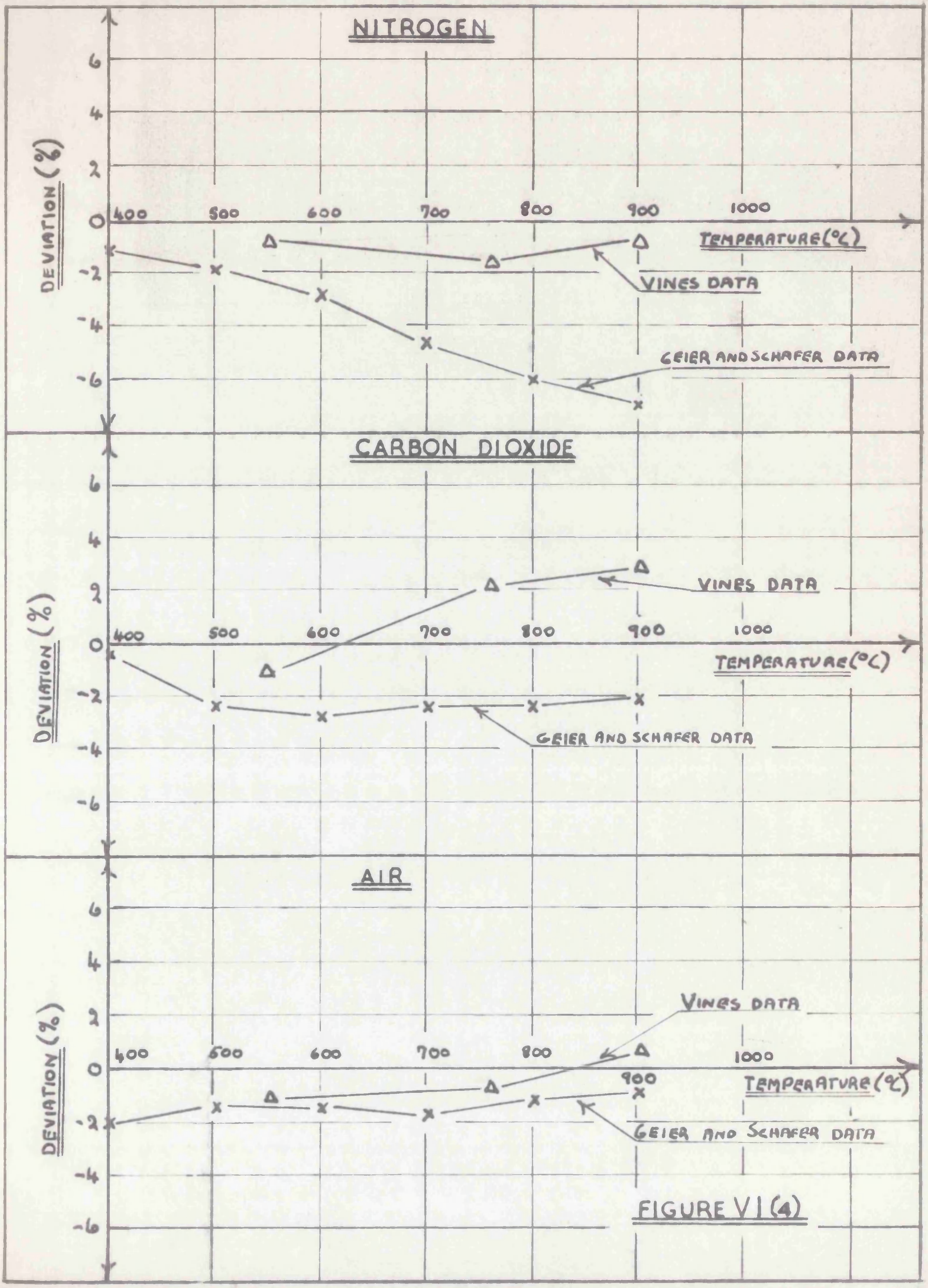

NITROGEN
CARBON DIOXIDE
AIR
DEVIATION (%)
TEMPERATURE (°C)
400
500
600
700
800
900
1000
6
4
2
0
-2
-4
-6
VINES DATA
GEIER AND SCHAFER DATA

FIGURE VI(4)

figures it would appear that the values found by Geier and Schafer may be estimated to be some 2% - 3% low in the range 400 °C - 700 °C. Raising their corrected values for steam by this order of magnitude they become at 400 °C, 0.6% - 1.6% low, at 500 °C, 1.3 - 2.3% low, at 600 °C 1.9% - 2.9% low and at 700 °C, 2% - 3% low, when compared with Vargaftik and Zimina's data.

Considering now the work of Vines (12) it will be noted that in his original paper the two points which he obtained for steam at 270 °C and 560 °C are given as 40.4 10^{-5} W/cm°K and 71.6 10^{-5} W/cm°K respectively. In the later work of Keyes and Vines (10) it is stated that, due to an error in calibrating the cell, the values listed by Vines should all be reduced by 2.5%. Thus the reduced values are 39.4 10^{-5} W/cm°K and 69.8 10^{-5} W/cm°K at 270 °C and 560 °C respectively. In their most recent publication Vargaftik and Zimina (14) note that Vines did not correct his steam results for 'thermal jump' effects and from their calculations state that at 270 °C Vines' value should be raised by 1.5% and at 560 °C by 5%. However, in their calculations they have considered Vines' cell gap size as 1 mm. From the dimensions listed in his paper the gap size in Vines' cell was 2 mm. Thus the corrections to be applied for 'thermal jump' should be 0.75% at 270 °C and 2.5% at 560 °C. The corrected values are 39.7 10^{-5} W/cm°K and 71.6 10^{-5} W/cm°K at 270 °C and 560 °C respectively. At 270 °C the value is still in good agreement with Vargaftik and Zimina data being lower by only 1% but at 560 °C the corrected value is still 4.7% lower.

As was stated in Chapter I section (3) the correlating equation I (A) favoured by Keyes and Vines, covering the temperature range 100 °C - 700 °C was formulated using only one experimental determination, that of Vines at 560 °C, between 400 °C and 700 °C. It is the opinion of the author that the existence of one experimental value some 4.7% low at 560 °C does not constitute enough evidence to suggest that the lower atmospheric line is correct.

While it is true, as suggested by Keyes, that the high temperature values, favoured by the Russian correlation of 1958, appear to have been somewhat high it is the opinion of the author that it must surely be conceded that arguments are overwhelmingly in favour of the lower high temperature values now given by Vargaftik and associates, with which the experimental values found in this work are in close agreement. Quite clearly the higher values given in the 1958 correlation were due to the measurements performed by Vargaftik in 1948. Removal of this data shows the rest of the Russian experimental observations to be in good agreement.

VI (2) Correlation of Data

A new correlation of data for the temperature range 100 °C - 700 °C, Pressure = 1 atmosphere, was undertaken to include the experimental observations of this work. Only works in which most of the experimental points are within the tolerances agreed by the Sixth International Conference on the Properties of Steam are included.

These works are:-

Vargaftik (5) 1937, Vargaftik and Cleshchuk (7) 1946, Vargaftik and Smirnova (11) 1956 (both 'hot wire' and concentric cylinder methods) Vargaftik and Zimina (14) 1963, Venart (1) 1964, Keyes and Vines (10) 1966 and this work.

The above data was fitted by means of least squares analysis to an equation of the type favoured by Vargaftik and Zimina.

$$\lambda, \left({}^{W}/_{cm\,^{o}K\ 10^{5}} \right) = a + bt + ct^{2} + dt^{3} \qquad \text{.... VI (A)}$$

(where t = temperature (^{o}C) and a, b, c, and d are constants).

It was noted that an equation with four coefficients gave a good fit to the data. The addition of a few more coefficients did not serve to greatly reduce the standard deviation of the experimental points from the equation values.

The coefficients used are:-

$a = 1.74122028 \cdot 10^{1}$

$b = 5.61430692 \cdot 10^{-2}$

$c = 1.18244725 \cdot 10^{-4}$

$d = -6.1135884 \cdot 10^{-8}$

So that thermal conductivity may be easily evaluated in any appropriate units from this equation it may be given in dimensionless form as

$$\frac{\lambda_1}{\dfrac{P_c^{\frac{1}{2}} R^{\frac{2}{3}} K^{\frac{1}{3}}}{V_c^{1/6}}} = a_1 + b_1 \left(\frac{T}{T_c} \right) + c_1 \left(\frac{T}{T_c} \right)^2 + d_1 \left(\frac{T}{T_c} \right)^3 \qquad \text{.... VI (B)}$$

where $T_c = 647.3\ ^{o}K$ = the critical temperature

$P_c = 221.2\ 10^{5}\ {}^{N}/_{M^2}$ = the critical pressure

$V_c = 3.17 \; 10^{-3} \; M^3/Kg$ = the critical volume

$R = 461.51 \; J/kg^oK$ = the gas constant

$k = 1.38041 \; 10^{-23} \; J/^oK$ = Boltzman constant.

Thus $$\frac{P_c^{\frac{1}{2}} R^{\frac{2}{3}} K^{\frac{1}{3}}}{V_c^{\frac{1}{6}}} = 1.75794841 \, . \, 10^{1} \left\{ W/cm^oK \times 10^5 \right\}$$

The coefficients used are

$a_1 = 6.90864037 \, . \, 10^{-1}$

$b_1 = -8.15161839 \, . \, 10^{-1}$

$c_1 = 4.01235341$

$d_1 = -9.43207448 \, . 10^{-1}$

The same data was also fitted to an equation of the type favoured by Keyes (10)

$$\lambda_1 = \frac{G_1 \, T^{\frac{1}{2}}}{1 + \dfrac{G_2 \tau}{10^{G_3 \tau}}} \qquad \text{.... VI(C)}$$

(where T = temperature (^oK), $\tau = 1/T$ and G_1, G_2 and G_3 are constants).

This may be written in more convenient form as

$$\frac{T^{\frac{1}{2}}}{\lambda_1} = \frac{1}{G_1} + \frac{G_2}{G_1} \frac{\tau}{10^{G_3 \tau}}$$

The equation evaluated by means of least squares analysis was

$$\frac{T^{\frac{1}{2}}}{\lambda_1 \left\{ W/cm^oK x 10^5 \right\}} = 1.08572214 \, . \, 10^{-2} + 3.24580928.10^2 \frac{\tau}{10^{12\tau}} \qquad \text{...VI(D)}$$

This equation gave a good fit to the data the standard deviation of the experimental points from the equation values being 1.8%.

Equation VI (A) gave a better fit to the data the standard deviation of the experimental points from the equation values being 1.6% and this equation in dimensionless form VI(B) is recommended. The deviations of the experimental points from the equation values are shown in figure VI (5) and in table VI (1) the experimental and equation values are given. In table VI (2) rounded values given by equation VI (A) are presented. It is recommended that a tolerance of $\pm$ 2% be put on these values over the complete range 100 $^{\circ}$C - 700 $^{\circ}$C. In figure VI (6) comparison of the values recommended by Vargaftik and Zimina and the most recent N.B.S. correlation with equation VI (A) values is shown.

VI (3) Conclusions

(1) A complete thermal conductivity test rig, designed and developed by the author has been constructed.

(2) The apparatus may be used for accurate thermal conductivity measurements on gases in the temperature range 100 $^{\circ}$C – 700 $^{\circ}$C at atmospheric pressure.

(3) Utilising two concentric cylinder type cells, suitable for absolute measurements, designed by the author, the thermal conductivity of steam in the temperature range 100 $^{\circ}$C - 700 $^{\circ}$C at atmospheric pressure has been measured with a probable accuracy estimated to be within $\pm$ 1.5% - $\pm$ 2%.

(4) The results obtained confirm Russian observations.

(5) A new correlation of data has been undertaken by the author. The tolerances put on the equation accepted by the Sixth International Conference on the Properties of Steam were $\pm$ 3% for the range $100 \leqslant t(^{\circ}C) \leqslant 400$ and $\pm$ 4% for the range $400 < t(^{\circ}C) \leqslant 700$. For the equation given in this work a reduction to $\pm$ 2% for the complete range $100 \leqslant t(^{\circ}C) \leqslant 700$ is recommended.

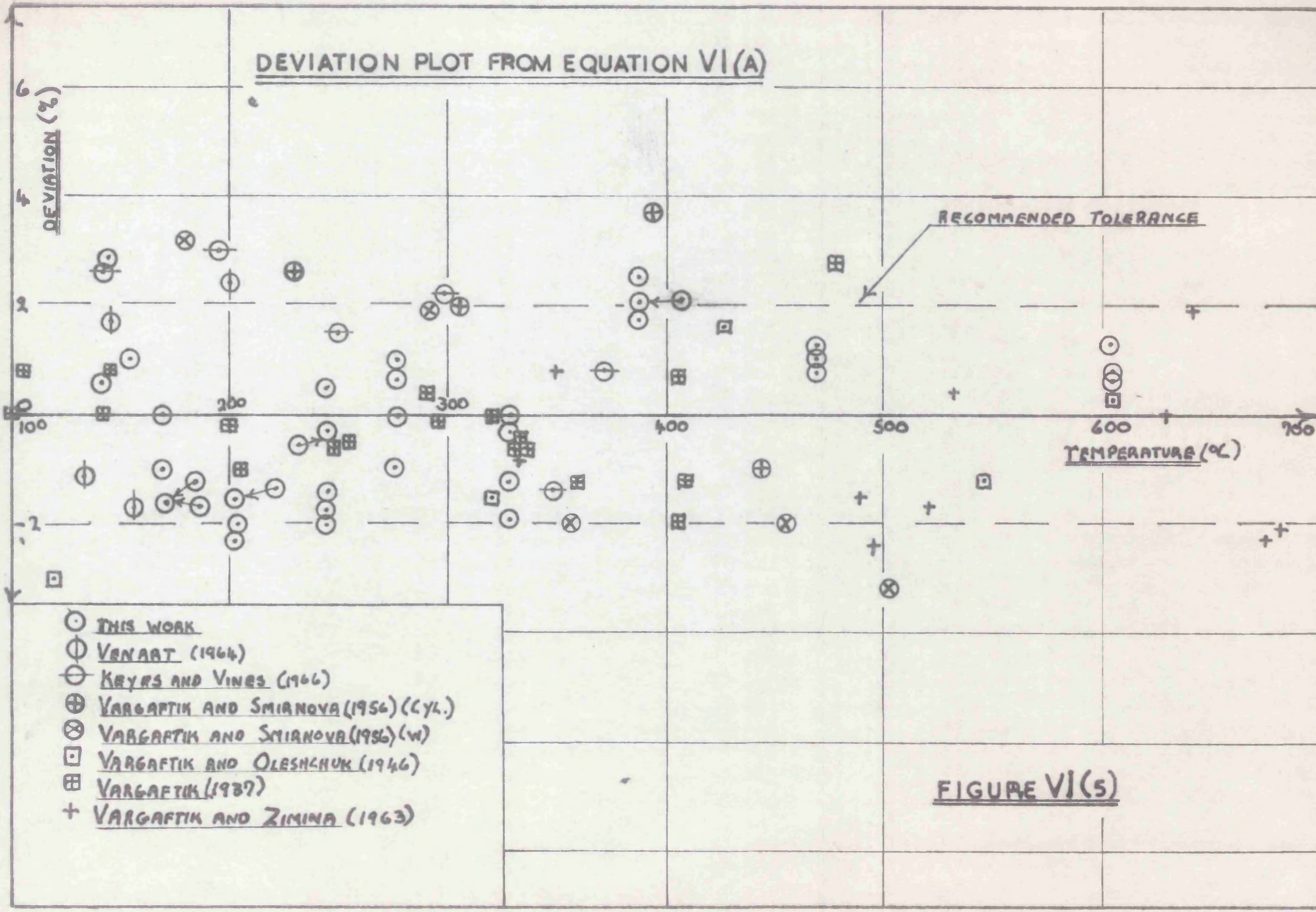

DEVIATION PLOT FROM EQUATION VI(A)
DEVIATION (%)
6
4
2
-2
100
200
300
400
500
600
700
TEMPERATURE (°C)
RECOMMENDED TOLERANCE
THIS WORK
VENART (1964)
KEYES AND VINES (1966)
VARGAFTIK AND SMIRNOVA (1956) (CYL.)
VARGAFTIK AND SMIRNOVA (1956) (W)
VARGAFTIK AND OLESHCHUK (1946)
VARGAFTIK (1937)
VARGAFTIK AND ZIMINA (1963)

FIGURE VI(5)

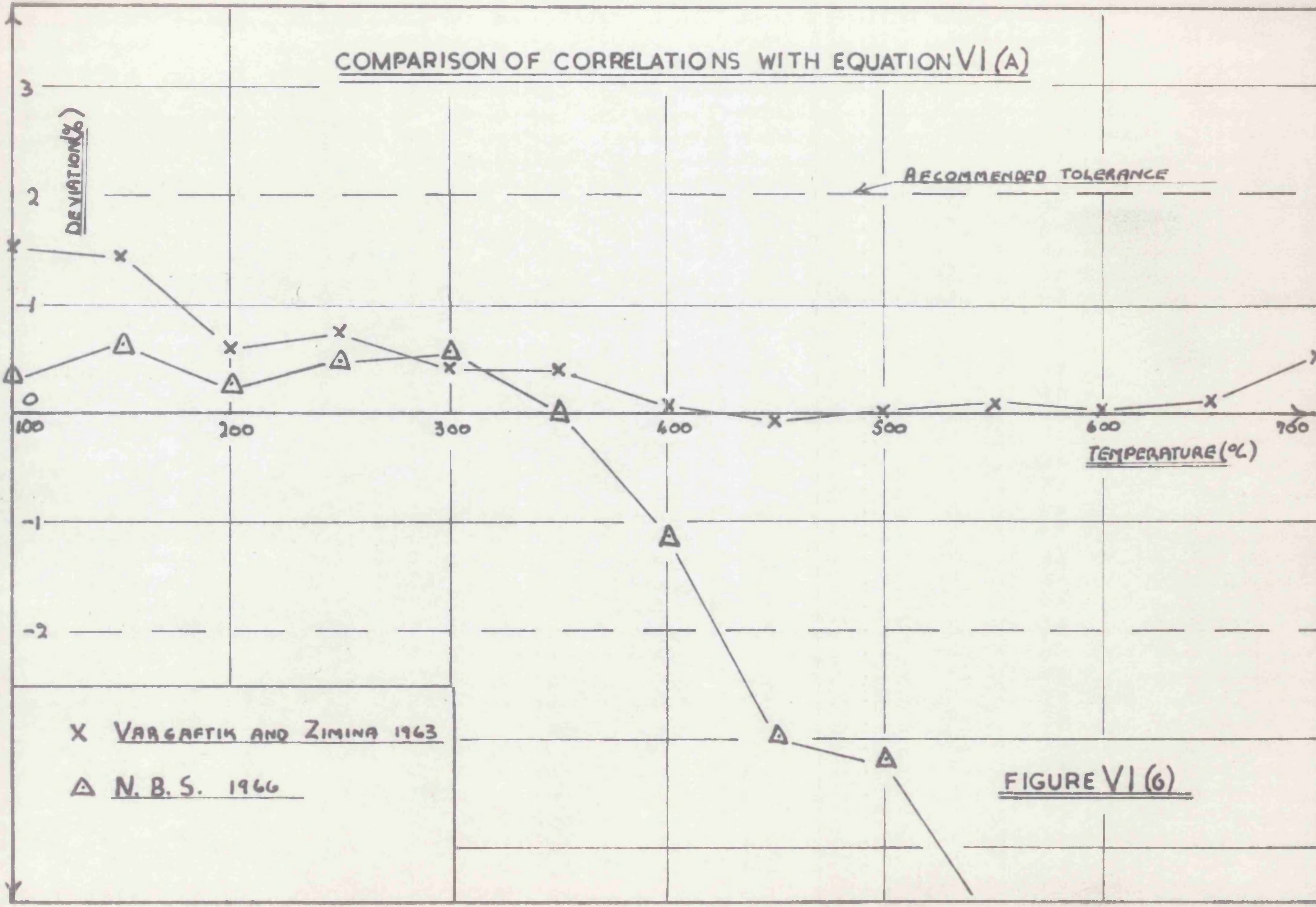
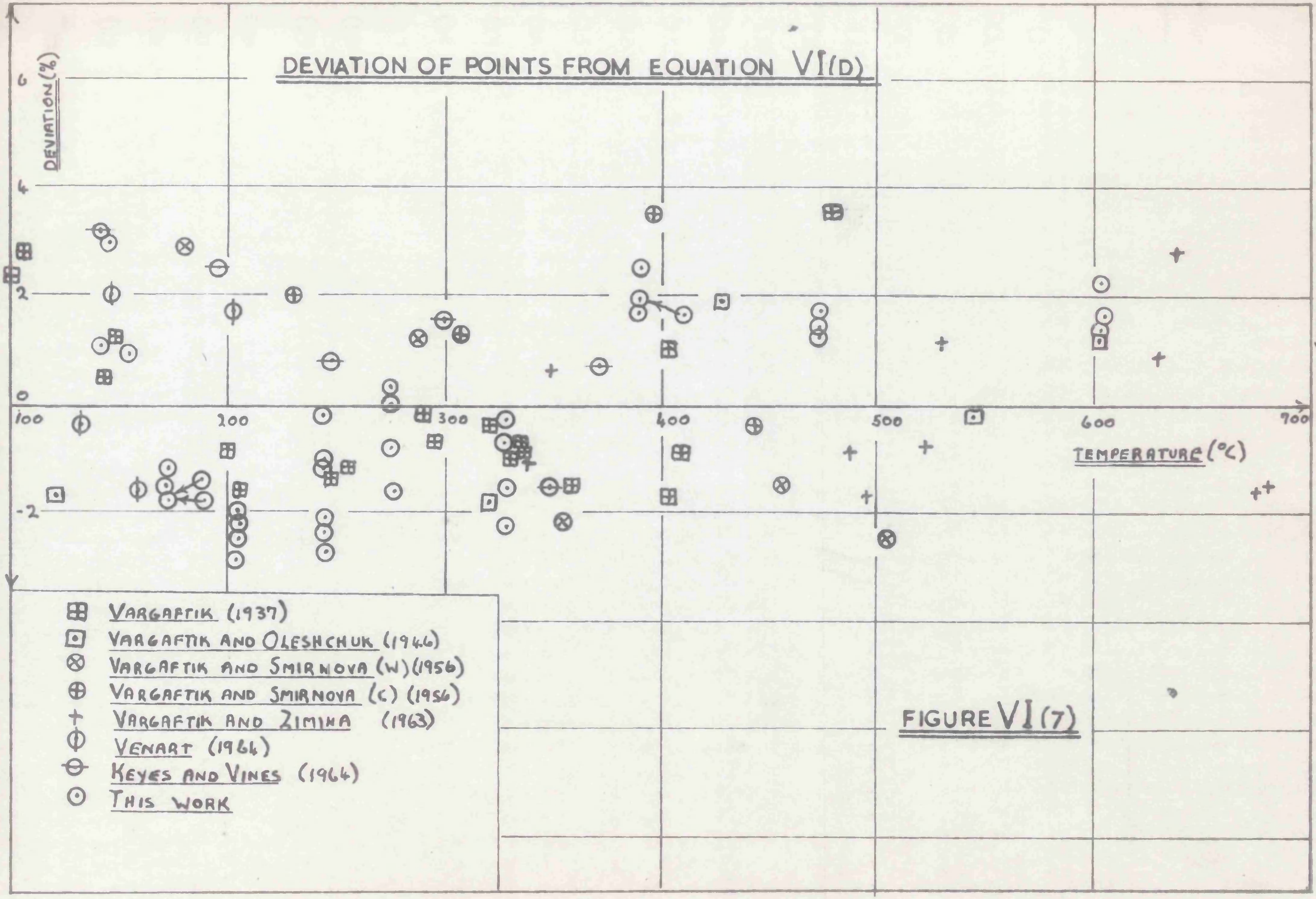

COMPARISON OF CORRELATIONS WITH EQUATION VI (A)
DEVIATION (%)
3
2
1
0
-1
-2
RECOMMENDED TOLERANCE
100
200
300
400
500
600
700
TEMPERATURE (°C)
X VARGAFTIK AND ZIMINA 1963
Δ N. B. S. 1966

FIGURE VI (6)



DEVIATION OF POINTS FROM EQUATION VI(D)
DEVIATION (%)
6
4
2
0
-2
100
200
300
400
500
600
700
TEMPERATURE (°C)
VARGAFTIK (1937)
VARGAFTIK AND OLESHCHUK (1946)
VARGAFTIK AND SMIRNOVA (W) (1956)
VARGAFTIK AND SMIRNOVA (C) (1956)
VARGAFTIK AND ZIMINA (1963)
VENART (1964)
KEYES AND VINES (1964)
THIS WORK

FIGURE VI (7)

TABLE VI (1)

Point No.*	Temperature (^{o}C)	λ_W observed ($^{W}/cm^{o}K \times 10^{5}$)	λ_W equation ($^{W}/cm^{o}K \times 10^{5}$)	Deviation	% Deviation
(1)	99.4	24.1	24.1	0	0
(2)	104.5	24.7	24.5	+0.2	+0.82
(3)	142.1	27.6	27.6	0	0
(4)	147.4	28.3	28.1	+0.2	+0.71
(5)	200.4	32.8	32.9	-0.1	-0.30
(6)	205.9	33.1	33.5	-0.4	-1.19
(7)	247.8	37.4	37.7	-0.3	-0.90
(8)	253.1	38.0	38.2	-0.2	-0.52
(9)	288.8	42.2	42.0	+0.2	+0.48
(10)	294.7	42.6	42.7	-0.1	-0.23
(11)	319.5	45.4	45.4	0	0
(12)	331.5	46.5	46.8	-0.3	-0.64
(13)	335.0	47.0	47.2	-0.2	-0.42
(14)	336.5	47.1	47.4	-0.3	-0.63
(15)	359.0	49.3	50.0	-0.7	-1.40
(16)	406.5	56.1	55.7	+0.4	+0.72
(17)	407.5	54.7	55.8	-1.1	-1.97
(18)	413.0	55.8	56.5	-0.7	-1.23
(19)	476.7	66.3	64.4	+1.9	+2.95
(20)	120.2	25.0	25.8	-0.8	-3.10
(21)	319.9	44.8	45.5	-0.7	-1.54
(22)	426.8	59.1	58.2	+0.9	+1.55
(23)	547.8	72.7	73.6	-0.9	-1.22

*See list on page 124

TABLE VI (1)

(cont'd)

(24)	600.6	80.7	80.5	+0.2	+0.25
(25)	179.6	32.0	31.0	+1.0	+3.23
(26)	287.5	42.7	41.9	+0.8	+1.91
(27)	356.8	48.7	49.7	-1.0	-2.01
(28)	454.9	60.4	61.7	-1.3	-2.11
(29)	504.8	65.8	68.0	-2.2	-3.24
(30)	230.6	36.9	35.9	+1.0	+2.79
(31)	308.1	45.0	44.1	+0.9	+2.04
(32)	394.0	56.1	54.1	+2.0	+3.70
(33)	442.2	59.5	60.1	-0.6	-1.00
(34)	337.4	47.1	47.5	-0.4	-0.84
(35)	349.8	49.3	48.9	+0.4	+0.82
(36)	523.4	69.2	70.4	-1.2	-1.70
(37)	532.3	71.8	71.6	+0.2	:0.28
(38)	631.4	84.6	84.6	0	0
(39)	638.5	87.2	85.6	+1.6	+1.87
(40)	487.0	64.7	65.7	-1.0	-1.52
(41)	494.0	65.0	66.6	-1.6	-2.40
(42)	675.0	88.2	90.4	-2.2	-2.43
(43)	680.0	89.0	91.0	-2.0	-2.2-

TABLE V1 (1) (cont'd)

(44)	134.0	26.6	26.9	-0.3	-1.12
(45)	148.0	28.6	28.1	+0.5	+1.78
(46)	159.0	28.6	29.1	-0.5	-1.72
(47)	201.0	33.8	33.0	+0.8	+2.42
(48)	139.25	28.1	27.4	+0.7	+2.55
(49)	195.95	33.5	32.5	+1.0	+3.08
(50)	249.20	38.4	37.8	+0.6	+1.59
(51)	299.45	44.1	43.2	+0.9	+2.08
(52)	349.35	48.2	48.9	-0.7	-1.43
(53)	370.85	51.8	51.4	+0.4	+0.78
(54)	142.4	27.8	27.6	+0.2	+0.72
(55)	143.8	28.5	27.7	+0.8	+2.89
(56)	158.6	29.3	29.0	+0.3	+1.03
(57)	170.3	29.6	30.1	-0.5	-1.66
(58)	170.6	29.6	30.1	-0.5	-1.66
(59)	171.4	30.2	30.2	0	0
(60)	171.6	29.9	30.2	-0.3	-0.99
(61)	172.8	29.8	30.3	-0.5	-1.65
(62)	205.9	32.8	33.5	-0.7	-2.09
(63)	206.2	32.7	33.5	-0.8	-2.39

TABLE V1 (1) (cont'd)

(64)	207.2	33.1	33.6	-0.5	-1.49
(65)	207.4	33.1	33.6	-9.5	-1.49
(66)	246.4	37.4	37.5	-0.1	-0.27
(67)	246.6	37.7	37.5	+0.2	+0.53
(68)	246.9	37.4	37.6	-0.2	-0.53
)69)	246.9	36.8	37.6	-0.8	-2.13
(70)	247.6	37.0	37.6	-0.6	-1.60
(71)	247.7	37.1	37.6	-0.5	-1.33
(72)	276.4	41.1	40.7	+0.4	+0.98
(73)	276.7	41.0	40.7	+0.3	+0.74
(74)	278.0	40.4	40.8	-0.4	-0.98
(75)	278.0	40.8	40.8	0	0
(76)	328.8	46.3	46.5	-0.2	-0.43
(77)	328.8	45.9	46.5	-0.6	-1.29
(78)	328.9	45.6	46.5	-0.9	-1.94
(79)	329.0	46.5	46.5	0	0
(80)	387.9	54.4	53.4	+1.0	+1.87
(81)	387.9	54.5	53.4	+1.1	+2.06
(82)	388.1	54.5	53.4	+1.1	+2.06
(83)	388.3	54.9	53.5	+1.4	+2.62
(84)	467.8	63.8	63.3	+0.5	+0.79
(85)	467.8	64.1	63.3	+0.8	+1.26

TABLE VI (1) (cont'd)

(86)	467.8	64.0	63.3	+0.7	+1.11
(87)	603.3	8.16	80.9	+0.7	+0.86
(88)	603.3	81.5	80.9	+0.6	+0.74
(89)	603.5	82.1	80.9	+1.2	+1.48

STD. DEVIATION:- 1.6%

Points	Reference
(1) - (19)	Vatgaftik 1937 (5)
(20) - (24)	Vargaftik and Oleshchuk 1946 (7)
(25) - (29)	Vargaftik and Smirnova 1956 (hot wire method) (11)
(30) - (33)	Vargaftik and Smirnova 1956 (concentric cylinder method) (11)
(34) - (43)	Vargaftik and Zimina 1963 (14)
(44) - (47)	Venart 1964 (1)
(48) - (53)	Keyes and Vines 1964 (10)
(54) - (89)	This work

TABLE V1 (2)

Values given by Equation V1 (A)

$T(^{o}C)$	$\lambda_1\ (^{W}/_{cm}\,^{o}K,\ 10^{5})$
100	24.1
150	28.3
200	32.9
250	37.9
300	43.2
350	48.9
400	54.9
450	61.1
500	67.4
550	73.9
600	80.5
650	87.1
700	93.7

Acknowledgement

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Appendix (1)

Correction for Current in Volt Ratio Box

The heat input to the emitter central heater is determined from the equation (see figure A(1)).

$$q = X V_e \left(\frac{v_i}{R_{STD}} - \frac{X V_e}{R_B} \right)$$

(where q = heat input, X = reduction factor for volt ratio box, v_i = voltage across standard resistor, R_{STD} = resistance of standard resistor, V_e = measured voltage across heater and R_B = resistance of the box).

$$q_{MEASURED} = X V_e \frac{v_i}{R_{STD}}$$

$$\therefore \text{ correction} = \left[\frac{X V_e \frac{v_i}{R_{STD}} - X V_e \left(\frac{v_i}{R_{STD}} - \frac{X V_e}{R_B} \right)}{X V_e \frac{v_i}{R_{STD}}} \right] . 100\%$$

$$= \frac{X V_e}{R_B} . \frac{R_{STD}}{v_i} . 100\%$$

inserting a typical set of values:-

$$\text{correction} = \frac{\frac{11.18_8}{9{,}997.1}}{0.2008} . 100\%$$

$$= \underline{\underline{0.56\%}}$$

POWER MEASUREMENT CIRCUIT

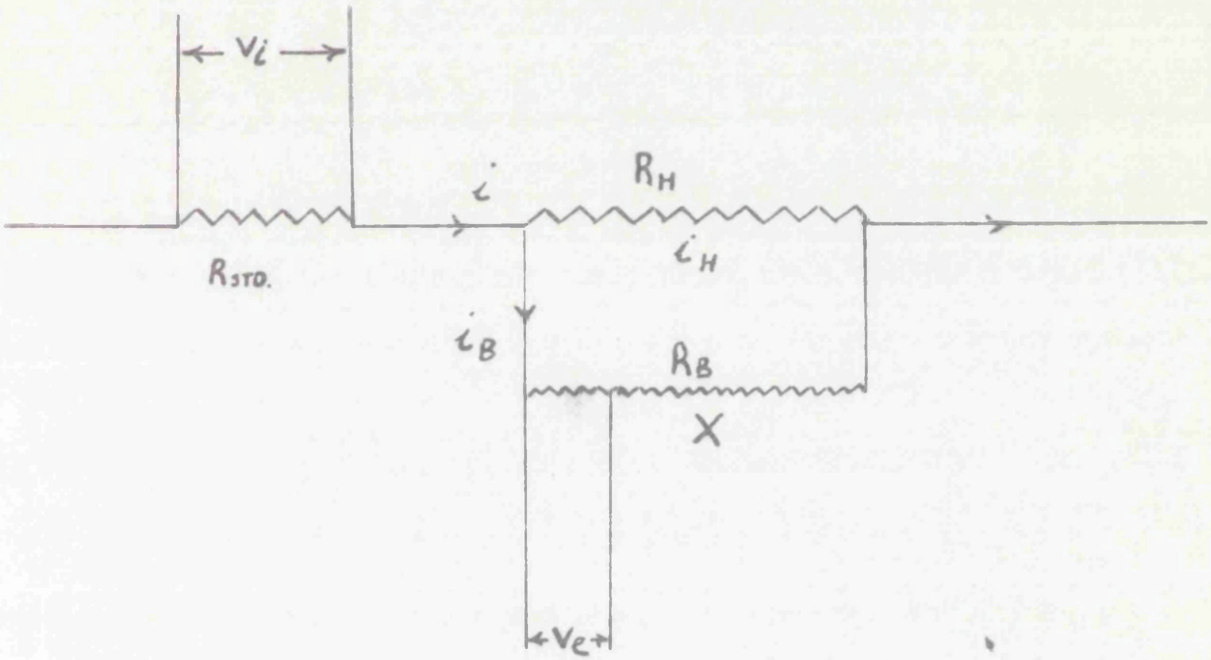

FIGURE A(1)

Appendix (2)

Influence of Axial Heat Flow

A series of tests were carried out at a mean temperature of 210°C to assess the influence of axial flow on conductivity determinations. The heat input to the emitter was kept constant (at approximately the smallest heat flow used in experiments) and the heat input to the guard heaters adjusted so that the cell temperatures were out of balance. The influence of this out of balance on the measured value of the thermal conductivity of the test gas was noted. This was done for several different degrees of out of balance and a plot of the percentage change in measured conductivity against out of balance was drawn. See figure A(2).

As a check on these values the influence of heat flow from the ends of the emitter was also calculated using the equations outlined in appendix (B) Section (3). From figure A(2) it can be seen that the calculated values agree well with those found experimentally.

AXIAL HEAT FLOW TESTS

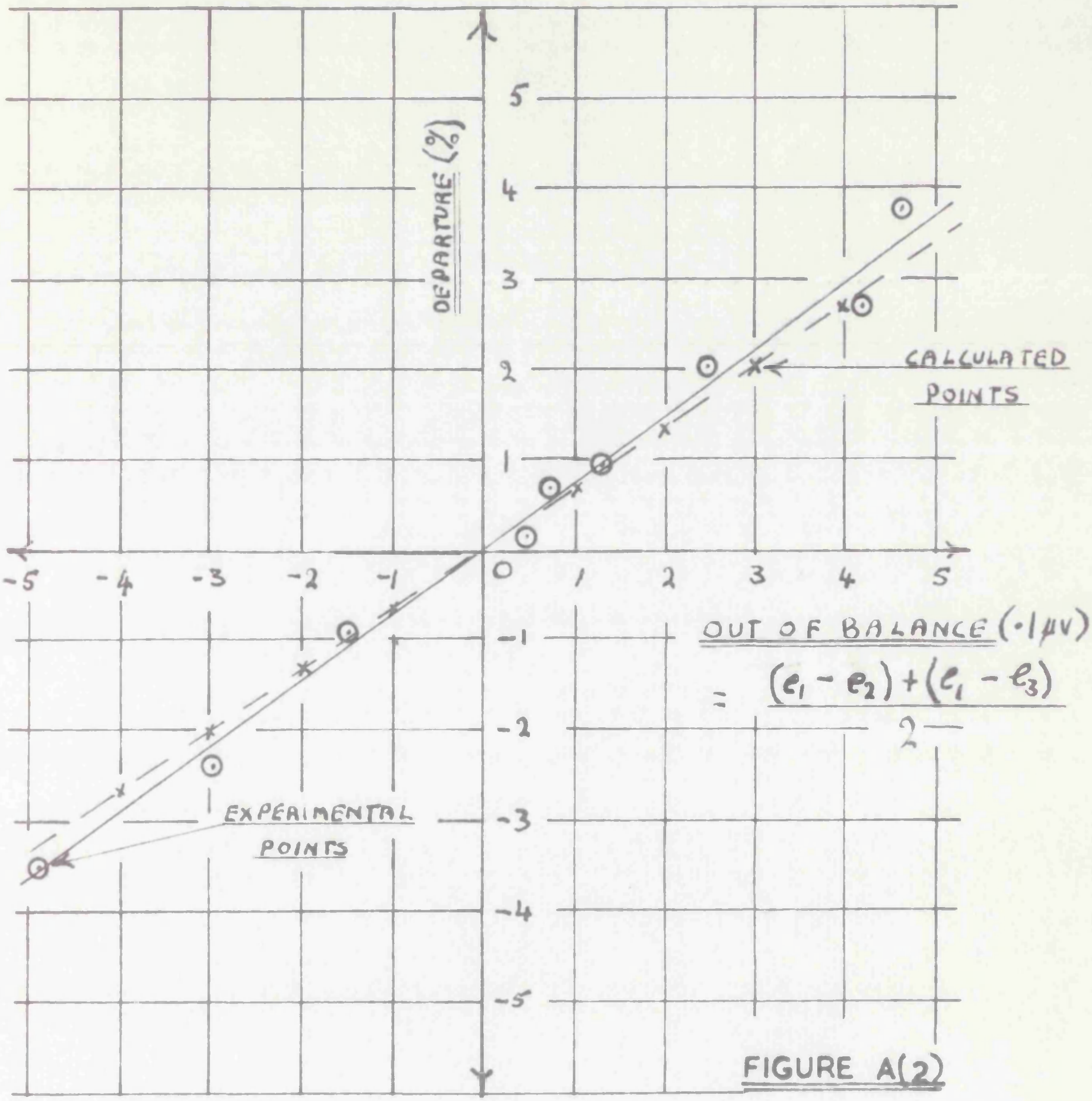

FIGURE A(2)

e_1 = E.M.F. OF EMITTER CENTRE THERMOCOUPLE

e_2 = E.M.F. OF UPPER HEAT GUARD THERMOCOUPLE

e_3 = E.M.F. OF LOWER HEAT GUARD THERMOCOUPLE

Appendix (3)

Joule Heat

When assessing the heat input to the emitter account had to be taken of the small amount of Joule heat generated in the heater leads which were located along the measurement section of the heater. The leads causing this effect were the positive current lead to the lower guard heater and the negative current lead from the lower guard heater and centre heater. These leads passed along the complete length of the measurement section. The resistance of the appropriate length of each of the wires, measured using a Wheatstone Bridge Circuit, was found to be 0.0229 Ω at 20°C. The variation of resistance of the wires with temperature was taken from data compiled by Smart A(3) 1.

The value of this correction, which was calculated at each temperature and heat flow at which measurements were made, was found by estimating the product $i^2 R_T$ for each of the wires (where i represents the current flowing in each wire and R_T is the resistance of each wire at temperature T).

Typical value was as follows:-

At T = 170.3°C inserting appropriate measured current values and calculated resistance value.

$$\Sigma i^2 R_T = 0.306 \times 0.036$$

$$= \underline{\underline{0.01102 \text{ watts}}}$$

The currents were measured by means of instruments provided in the electrical circuits described in Chapter II section (3)

Reference

A(3) 1 Smart J.S. 'Metals Handbook' Pub.American Soc.for Metals. Cleveland, Ohio, 1948 P.903

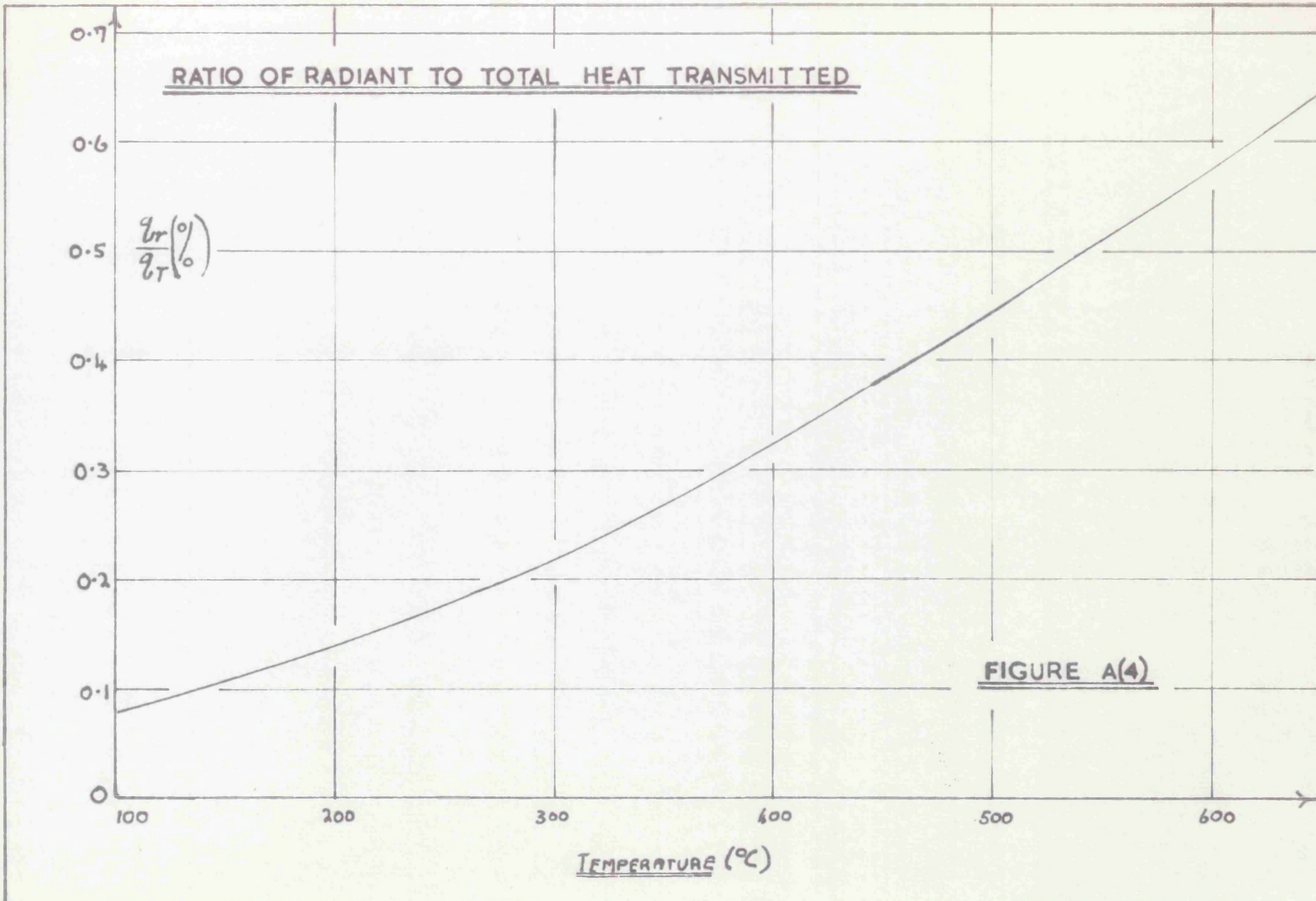
RATIO OF RADIANT TO TOTAL HEAT TRANSMITTED
$\frac{q_r}{q_T}$ (%)
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
100
200
300
400
500
600
TEMPERATURE (°C)

FIGURE A(4)

Appendix (4)

Radiation Correction

The radiant heat component at each temperature at which measurements were made was taken into account by calculating its magnitude from the equation.

$$q_r = \frac{\sigma \, 2\pi r_1 L \left(T_1^4 - T_2^4\right)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)} \qquad \ldots \text{A}(4)(1)$$

where $\epsilon = 0.013 + 3.10^{-5} t.$

index of refraction $n = 1$

(where σ = Stefan Boltzman constant; r_1 = radius of emitter; r_2 = radius of receiver; L = length of measurement section; T_1 = temperature of the emitter ($^{\circ}$K); T_2 = temperature of the receiver($^{\circ}$K); ϵ = emissivity of cell surfaces; t = temperature ($^{\circ}$C)

The ratio of radiant to total heat transmitted is shown in figure A(4) for the temperature range to be covered by this experimental work and was calculated from

$$\frac{q_r}{q_T} = \frac{\dfrac{\sigma r_1 \left(T_1^4 - T_2^4\right)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)}}{\dfrac{\sigma r_1 \left(T_1^4 - T_2^4\right)}{\frac{1}{\epsilon} + \frac{r_1}{r_2}\left(\frac{1}{\epsilon} - 1\right)} + \dfrac{\lambda \left(T_1 - T_2\right)}{\log_e \frac{r_2}{r_1}}} \qquad \ldots \text{A}(4)(2)$$

For the brass cell values of the emissivity of the cell surfaces were obtained from M^cadams (A(4) 1). The radiant heat component may be estimated to be 0.43% of the total heat transferred at 143.8°C and 142.4°C and 0.46% of the total heat transferred at 158.6°C.

Reference

A(4) 1. M^c^Adams, W.H. 'Heat Transfer' pub. McGraw Hill 3rd edition P.473, 1954

RATIO OF TEMPERATURE DROP IN CELL MATERIAL TO MEASURED TEMPERATURE DIFFERENCE

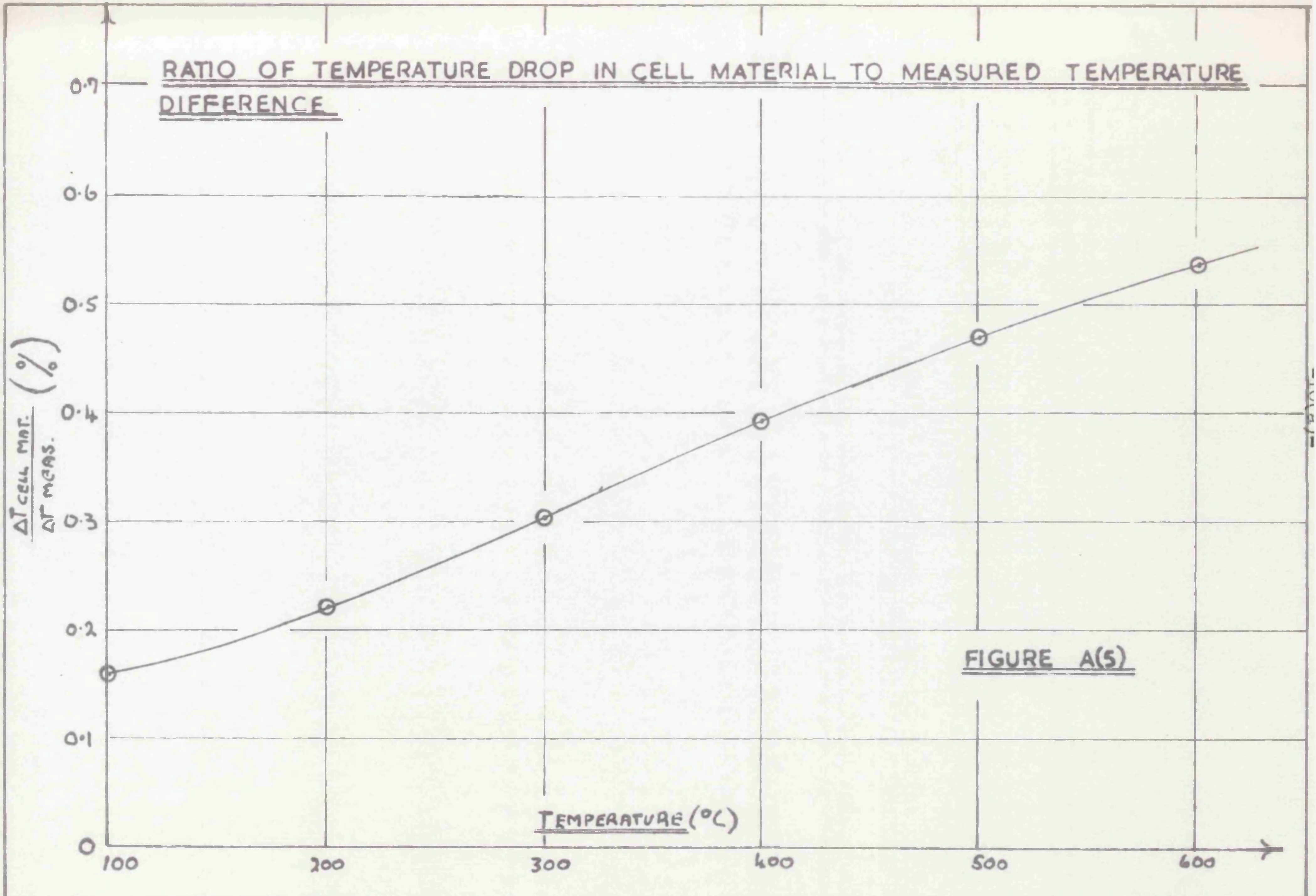

FIGURE A(5)

Appendix (5)

Estimation of Temperature Drop in Cell Material

The temperature drop in the cell material may be estimated from

$$\Delta T \text{ cell material} = \frac{q}{2\pi L \lambda_{s_1}}\left(\log_e \frac{r_1}{r_i} + \log_e \frac{r_o}{r_2}\right) \quad \ldots A(5)1$$

(where q = heat input to the emitter, L = length of emitter measurement section; λ_{s_1} = thermal conductivity of silver; r_1 = radius of emitter; r_2 = internal radius of receiver; r_i = radius on which emitter thermocouples are spaced: r_o = radius on which receiver thermocouples are spaced).

$$\therefore \frac{\Delta T \text{ cell mat}}{\Delta T \text{ measured}} \% = \frac{\frac{1}{\lambda_{s_1}}\left(\log_e \frac{r_1}{r_i} + \log_e \frac{r_o}{r_2}\right).100}{\frac{1}{\lambda}\log_e \frac{r_2}{r_1} + \frac{1}{\lambda_{s_1}}\left(\log_e \frac{r_1}{r_i} + \log_e \frac{r_o}{r_2}\right)} \quad \ldots A(5)2$$

(where λ = the thermal conductivity of steam)

inserting values for r_2 , r_1 , r_i , and r_o

$$= \frac{0.4913 \times 100}{\frac{\lambda_{s_1}}{\lambda}\,0.01955 + 0.4913} \%$$

Using values for the thermal conductivity of silver found in reference A(5)1 this ratio is plotted in figure A(5) against temperature.

For the brass cell inserting appropriate values

$$\frac{\Delta T \text{ cell mat}}{\Delta T \text{ measured}} \% = \frac{0.4682 \times 100}{\frac{\lambda_b}{\lambda}\, 0.0426 + 0.4682}$$

(where λ_b = the thermal conductivity of brass).

Values of the thermal conductivity of brass were taken from reference A(5)2. This effect accounted for 0.29% of the measured temperature difference at 142.4°C and 143.8°C and 0.30% of the measured temperature difference at 158.6°C.

References:

A (5) 1 Addicks, L. 'Silver in Industry' pub. Reinhold Corp. New York, 1940

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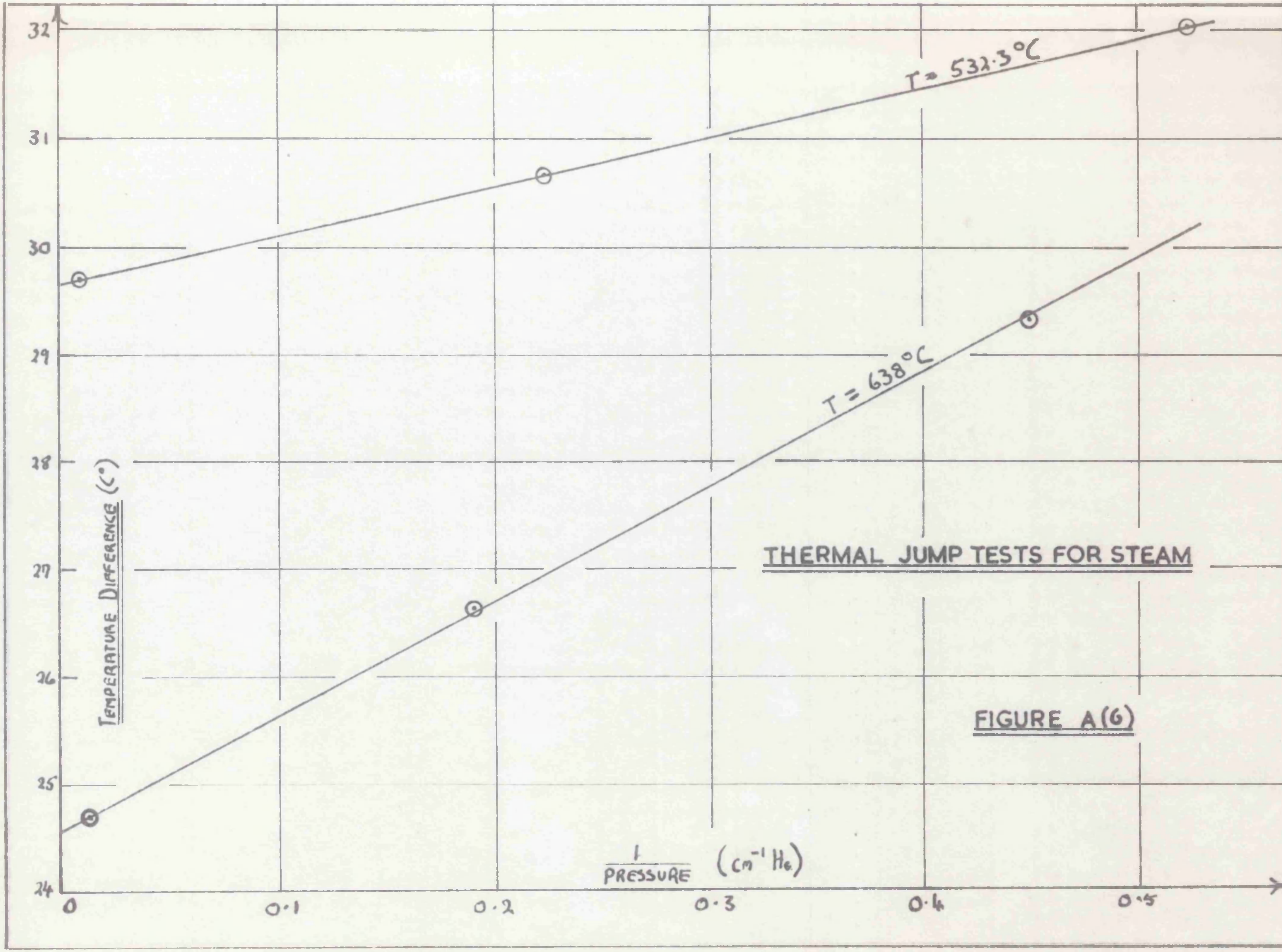

THERMAL JUMP TESTS FOR STEAM

FIGURE A(6)

Appendix (6)

The Influence of 'Thermal Jump'

Corrections to the measured temperature difference to take into account the effects of 'thermal jump' (see chapter II section 4(A)), were made at temperatures of 468°C and 604°C. At lower temperatures calculation showed the effect to be negligibly small.

Vargaftik and Zimina (A(6) 1), (A(6) 2) have drawn up a series of curves for a hot wire cell from which this effect may be calculated for both nitrogen and steam for either a concentric cylinder or a hot wire apparatus. The work of Rothman (A(6) 3), who used a silver concentric cylinder cell to measure the thermal conductivity of gases at high temperatures, may also be used. Using either the work of Rothman or Vargaftik and Zimina the same corrections are obtained.

According to Vargaftik and Zimina it can be shown, using Rothman's derived equations, that for a hot wire cell and a concentric cylinder cell, in which the accommodation coefficients of the gas with respect to the wire and cylindrical surfaces are similar, at the same temperature and pressure, measuring the same gas, it can be estimated that

$$N = \frac{(\delta t_c)_{cyl}}{(\delta t_c)_{wire}} = \frac{2 r_1 \log_e \frac{r_2}{r_1}}{S}$$

(where $(\delta t_c)_{cyl}$ and (δt_c) wire, are the percentage errors in temperature difference caused by ignoring the effects of 'thermal jump' in the concentric cylinder and hot wire cells respectively ; r_1 = radius of the wire and r_2 = internal radius of the receiver in the hot wire cell and δ = the width of the cylindrical gap in the concentric cylinder cell.

Inserting the appropriate values for the radii of the cell of Vargaftik and Zimina and the gap width of this cylindrical cell

$$N = \frac{0.157 \ \log_e 25.9235}{0.204} = \underline{\underline{2.505}}$$

Thus the corrections found by reference to figure A(5), where the lines of Vargaftik and Zimina are shown, must be multiplied by the factor 2.505 to apply to this cell.

At 468°C the measured temperature difference has to be reduced by 0.1% and at 604°C by 0.8%. These values are arrived at by reference to calculations by the same method for the isotherms shown in figure A(6).

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A (6) (2) Vargaftik,N.B. and Zimina Teploenergetika Vol.11,No.12 P.84,(1964)

A (6) (3) Rothman,A.J. 'Thermal Conductivity of Gases at High Temperatures', U.S.Atomic Energy Commission 1954.

Appendix (7)

Calculation of the Cell Constant

The cell constant, for each cell, was calculated using the dimensions quoted in Table III (1). The thermal expansion of the silver cell was taken into account using the equation mentioned in chapter II section 4(C). This equation was obtained from data compiled by Wise (A (7) 1). The values of the natural logarithms used were taken from Chambers Six Figure Mathematical Tables volume II. (A (7) 2). The thermal expansion of the brass cell was taken into account from data supplied by Smart (A (7) 3).

For the silver cell inserting the appropriate dimensions

$$\text{Constant} = \frac{\log_e \ 1.019740}{6.28318.\ 7.497_1 (1+19.494.10^{-6}t + 1.0379.10^{-9}t^2 + 2.375.10^{-12}t^3).}$$

For the brass cell

$$\text{Constant} = \frac{\log_e \ 1.04353_3}{6.28318.\ 7.497\ (1 + 20.3.10^{-6}t)}$$

(where t = temperature ($^{\circ}$C)).

References

A (7) 1. Wise E.M. 'Properties of Silver' Metals Handbook.Pub. American Society for Metals, Cleveland,Ohio (1948),P.1110.

A (7) 2. ComrieL.J. Chambers Six Figure Mathematical Tables, Volume II. Pub. Chambers,Edinburgh(1948)

A (7) 3. Smart,J.S. 'Properties of Brass' Metals Handbook.Pub. American Society for Metals, Cleveland,Ohio, (1948),P.917

Appendix (8)

Calibration of Volt Ratio Box

A check on the calibration of the volt ratio box used was carried out to check the nominal ratio as specified by the manufacturers. The nominal voltage reduction factor of the box and the total resistance were checked against the class S.1000 coils of the Smith Bridge used in laboratory.

Table A (8)

Calibration of Volt Ratio Box (Test Temperature 20°C)

Nominal Reduction Factor	Measured Ratio
100	99.980_5
200	199.944_8
300	299.928_6
400	399.910_5
500	499.891_0

Resistance of Box

Nominal Resistance	Measured Resistance
10,000 Ω	9997.1Ω $\pm$ ·1 Ω

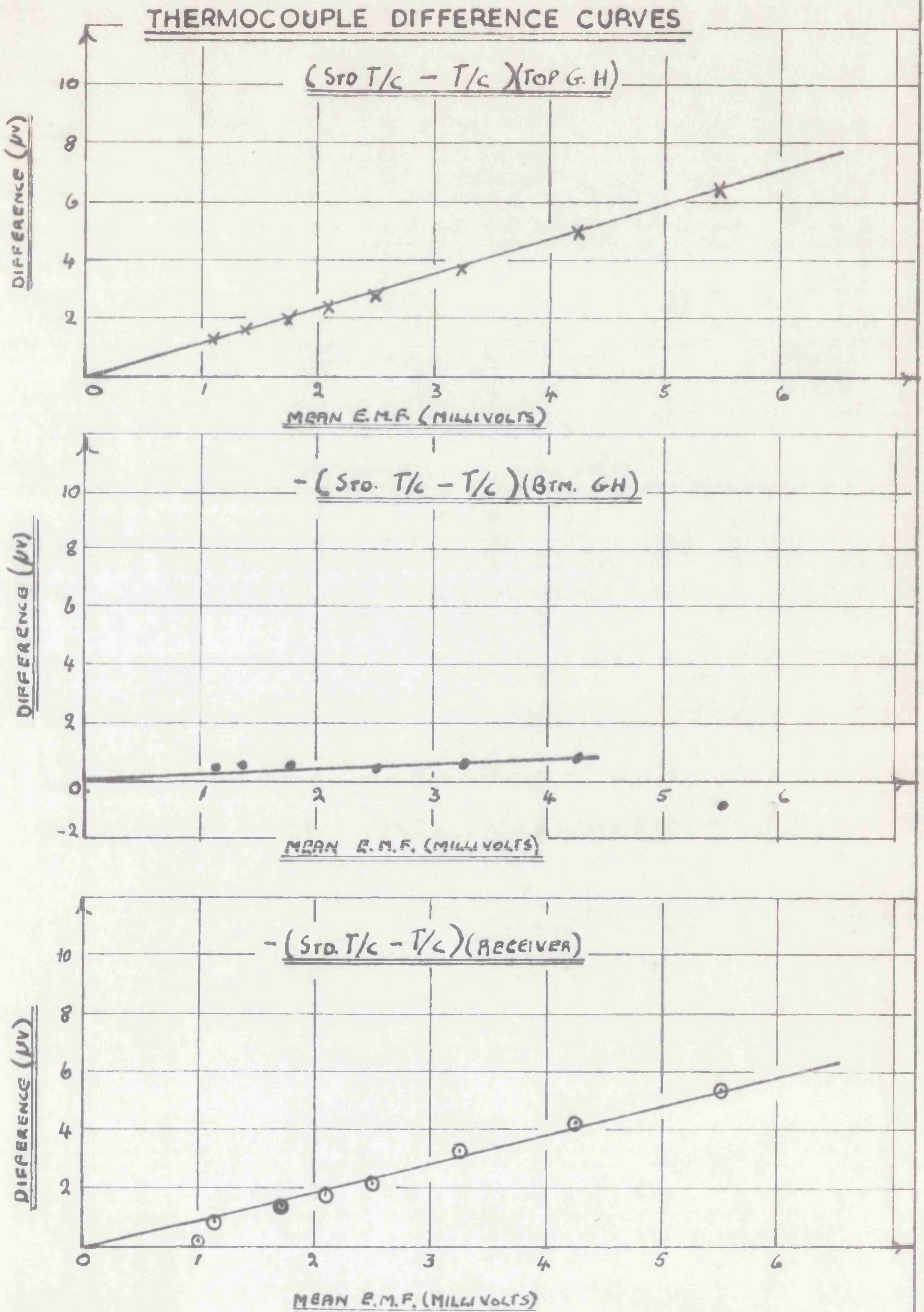
THERMOCOUPLE DIFFERENCE CURVES
(STD T/C – T/C)(TOP G. H)
DIFFERENCE (μV)
10
8
6
4
2
0
1
2
3
4
5
6
MEAN E.M.F. (MILLIVOLTS)
–(STD. T/C – T/C)(BTM. GH)
DIFFERENCE (μV)
10
8
6
4
2
0
-2
1
2
3
4
5
6
MEAN E.M.F. (MILLIVOLTS)
–(STD. T/C – T/C)(RECEIVER)
DIFFERENCE (μV)
10
8
6
4
2
0
1
2
3
4
5
6
MEAN E.M.F. (MILLIVOLTS)

FIGURE A(9)1

Appendix (9)

Calibration Check and Differencing of Thermocouples

The thermocouples which were used were Johnson and Matthey Pt - Pt.13% Rh. thermocouples and were made from the same batch of carefully annealed wire. They were carefully differenced, at each temperature, at which thermal conductivity measurements were made to take into account the slightly different temperature e.m.f. characteristics of each couple. The procedure was as described in Chapter lV section (1) each of the thermocouples being differenced from a 'standard' thermocouple. The curves obtained are as shown in figure A (9) 1, where it can be seen that the differences found were small and that in each case a good fit to a straight line was obtained. Deviation from a straight line was noted for the final difference obtained for the bottom guard heater thermocouple. This deviation was probably due to a slight straining of the wires which occurred when checks by interchanging were made at this temperature. Repeated checks were carried out which confirmed that this difference remained both accurate and consistent. Each of the e.m.f. measurements made during steady state thermal conductivity determinations was corrected to take into account these differences.

Calibration of the standard thermocouple was checked by calibrating against an N.P.L. certificated platinum resistance thermometer. The thermocouple and resistance thermometer were inserted closely together, into a solid copper block which was placed in the calibration furnace. Readings both 'direct' and 'reverse' were taken at 100 C° intervals over the range in which thermal conductivity measurements were made. The circuit used was as shown in figure A (9) 2. The standard resistance used was a 25 Ω class S. N.P.L. certificated resistance and the current used was varied between 1 and 2 milliamps. Any errors due to self heating effects were small. These tests showed that uncertainty in overall temperature measurement was less than 0.3%.

RESISTANCE THERMOMETER CIRCUIT

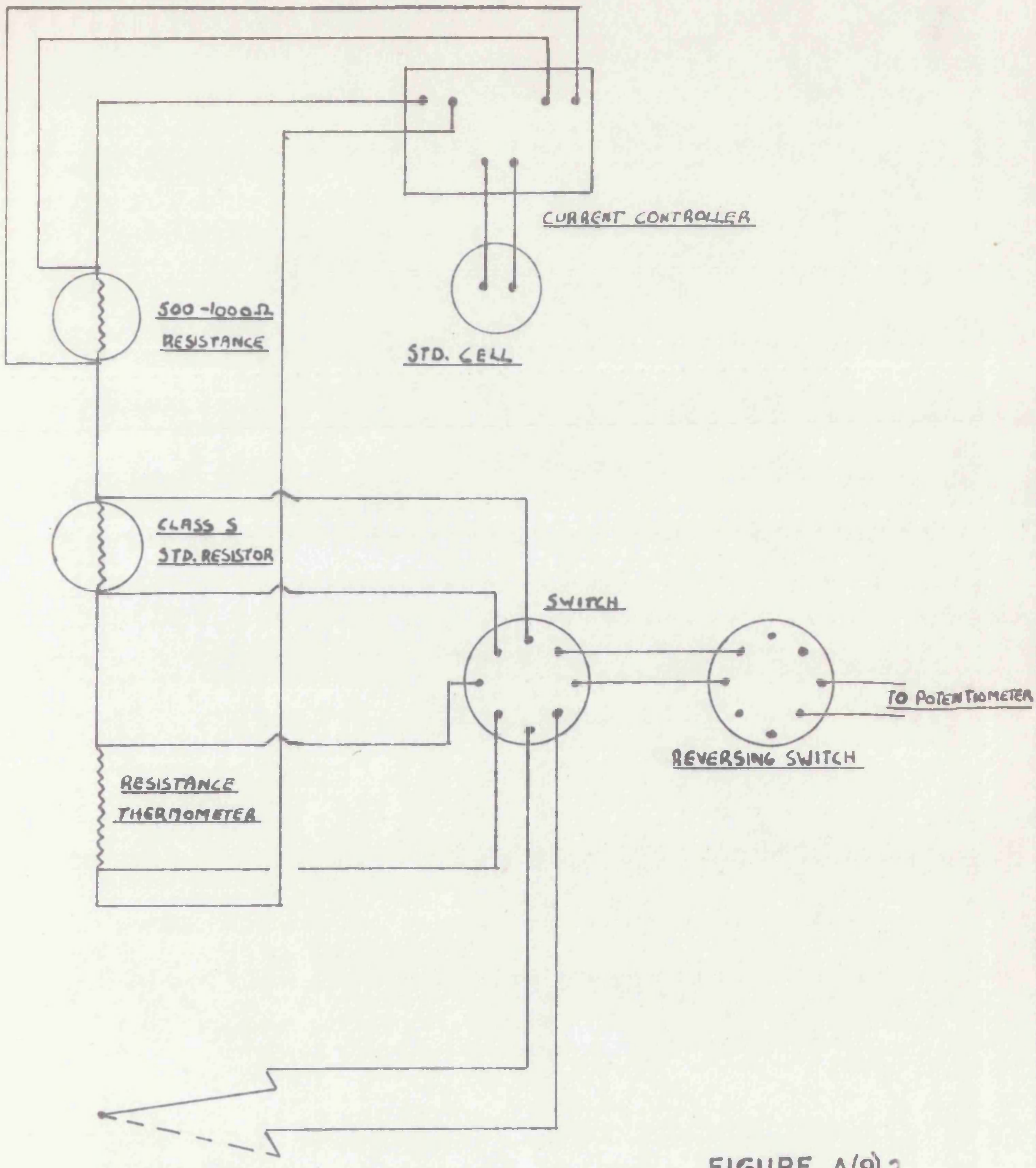

FIGURE A(9) 2

Appendix(10)

Purity of Water used in experiments

The water used in these experiments was demineralised by using the water purification apparatus supplied to the steam generating plant of the Laboratory. The specific conductivity of each of the water samples, used to generate the steam used in the experimental tests, was carefully determined and found to be some 0.06 micromhos in all cases.

APPENDIX (A)

Reprinted from the International Journal of Heat
and Mass Transfer, Vol.10, PP.737 - 744 (1967)

Appendix (A)

Int. J. Heat Mass Transfer. Vol. 10, pp. 737–744. Pergamon Press Ltd. 1967. Printed in Great Britain

NEW THERMAL CONDUCTIVITY MEASUREMENTS FOR ARGON, NITROGEN AND STEAM

T. J. S. BRAIN

University of Glasgow, Mechanical Engineering Research Annexe, Glasgow W.3

(*Received* 17 *October* 1966 *and in revised form* 1 *December* 1966)

Abstract—This paper describes the experimental measurement of the coefficient of thermal conductivity of argon and nitrogen in the range 100–300°C at atmospheric pressure utilising a guarded concentric cylinder cell made of silver.

Also given are results for argon, nitrogen and steam in the range 140–180°C at atmospheric pressure utilizing a concentric cylinder cell made of brass.

The results show good agreement with recent published values. The mean deviation of the points from the recently published correlations, for these gases, of Vargaftik and Zimina is some 1 per cent.

NOMENCLATURE

- λ, coefficient of thermal conductivity [W/cm°K];
- q, radial heat flow [W];
- r_1, radius of inner cylinder [cm];
- r_2, radius of outer cylinder [cm];
- L, length of measurement section [cm];
- T_1, temperature of the inner cylinder [°K];
- T_2, temperature of the outer cylinder [°K];
- ϵ, emissivity of the test cell material;
- σ, Stefan–Boltzmann constant [W/cm^2 (°K)^4];
- $q_{r\ \text{transparent}}$, heat transferred radially by radiation [W].

1. INTRODUCTION

THE AUTHOR has constructed a new test rig to measure the thermal conductivity of steam in the range 100–700°C at atmospheric pressure. So that experience could be gained in operating the apparatus and to confirm that the test rig could be used to obtain accurate thermal conductivity values it was decided to obtain first experimental values for two gases at moderately high temperatures.

Since the thermal conductivity of argon is well known in this range it was thought that argon would prove the most suitable gas to test the accuracy of the rig. Despite many measurements and correlations for the thermal conductivity of nitrogen there appear considerable divergencies in the published values in this range. It was therefore thought that new measurements for nitrogen would also prove useful.

2. METHOD OF MEASUREMENT

In these experiments a vertical coaxial cylinder apparatus with guard heaters was employed. Heat is generated in the inner cylinder and is passed radially through a narrow gas filled annulus to the surrounding receiving cylinder. In this case:

$$\lambda = \frac{q \log_e r_2/r_1}{2\pi L(T_1 - T_2)}.$$

3. APPARATUS

A sketch of the conductivity cell used is shown in Fig. 1. The cell is of similar design to that used by such experimenters as Venart [1] and Vines [2]. The brass and silver cells are of identical construction but of slightly different dimensions

Appendix (A)

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A sketch of the conductivity cell used is shown in Fig. 1. The cell is of similar design to that used by such experimenters as Venart [1] and Vines [2]. The brass and silver cells are of identical construction but of slightly different dimensions as shown in Table 1. Only the silver cell will be described.

The cell consists of two cylinders made of pure silver. The inner cylinder is divided into three sections, the emitter E and two guard

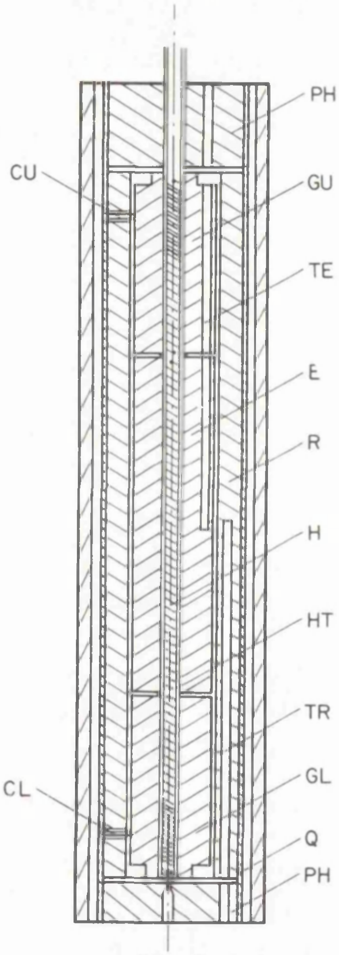

FIG. 1. Thermal conductivity cell.

cylinders GU and GL. In the gaps between the emitter and the guard cylinders additional support is provided by six small 1-mm-dia. silver pins, three spaced at 120° on a 1·5 cm P.C.D. at the top and bottom gaps (not shown in diagram). The width of the heat guard gaps is 1 mm. Surrounding the inner cylinder is the receiver R. The emitter is located inside the receiver by means of six mica spacers three spaced uniformly around near the top, CU, and three similarly spaced near the bottom, CL. The spacers are held in position by means of grub screws.

Table 1. Cell dimensions

(a) Silver cell	
diameter of emitter:	2·0433 ± 0·00025 cm
diameter of receiver:	2·0836 ± 0·00006 cm
length of measurement section:	7·50 ± 0·015 cm
O.D. of receiver:	3·0 cm
surface finish:	4×10^{-6} in
(b) Brass cell	
diameter of emitter:	1·9202 ± 0·00025 cm
diameter of receiver:	2·0038 ± 0·0001 cm
length of measurement section:	7·50 ± 0·015 cm
O.D. of receiver:	3·0 cm
surface finish:	4×10^{-6} in

All measurements made at a temperature of 20°C.

The complete cell is mounted in a precision bore quartz tube Q. The quartz tube on each side of the cell is fitted with accurately machined blocks of fired pyrophyllite PH.

The heater H is a press fit inside the slim stainless steel heater tube HT of O.D. 3·2 mm. The heater consists of a six bore, 1·8-mm dia. alumina insulator, bore size 0·4 mm, on which the main and guard heater windings are wound. The windings are of 41 s.w.g. Nichrome wire and are cemented in position by a high temperature refractory cement. Current carrying copper leads (32 s.w.g.) are silver soldered to the ends of the three windings and potential leads (36 s.w.g. chromel), are also attached to the ends of the main winding. The current and potential leads are carried to the outside of the furnace in the heater tube through the bores of the insulators. The main advantage of this heater construction is that with the cell guard heater temperatures matched, as they were in these experiments, to the temperature at the centre of the emitter axial heat exchange between individual heater sections is, if not eliminated, reduced to an extremely small value. The d.c. supply to the heaters is provided from two 72 V banks of heavy duty batteries. Any voltage between 2 V and 72 V can be selected. The power input to the emitter heater is obtained by measurements of the voltage drop across the heater, utilizing a potential divider, and the current flowing through the heater, by measuring the voltage drop across a standard resistor in series with the heater.

Thermocouple wells, TE and TR, are provided to enable measurement of the temperature difference across the gas gap to be made. Thermocouple wells are also provided in the heat guards so that the temperature of the heat guards can be accurately matched with the temperature at the centre of the emitter. The thermocouples are made from annealed 33 s.w.g. Pt – Pt – 13% Rh wires which are supported and insulated in slim two bore 1·2 mm-dia. alumina tubes. To avoid contamination the thermocouples are enclosed in thin-walled stainless steel tubes of O.D. 1·5 mm sealed at one end by means of small silver cylinders which are silver soldered to the ends of the stainless steel tubes. The hot junctions press against the silver end plugs which maintain close thermal contact in the thermocouple wells. From experiments carried out on these thermocouples it was concluded that any thermal gradient along the length of the thermocouples encountered in the thermal conductivity experiments had no measurable effect on the measured thermal e.m.f. The cold junctions are soft soldered to heavy copper leads which are attached to the potentiometer circuit. The soft soldered junctions are immersed in long glass tubes sealed at one end and filled with paraffin wax. The glass tubes are immersed in an ice bath which provides zero reference temperature. At all points between where they emerge from the furnace and the ice bath the wires are supported in thick P.V.C. sleeving to prevent undue straining.

A cross section of the thermostat assembly is shown in Fig. 2. It consists essentially of a high temperature refractory furnace tube FT on which three separate windings UW, CW, LW of 21 s.w.g. Nichrome wires are spaced and cemented in position. The current of the central winding CW is controlled by a C.N.S. S.R.$_2$ temperature controller. The platinum resistance thermometer TH which effects the control is placed, as shown, next to the central winding.

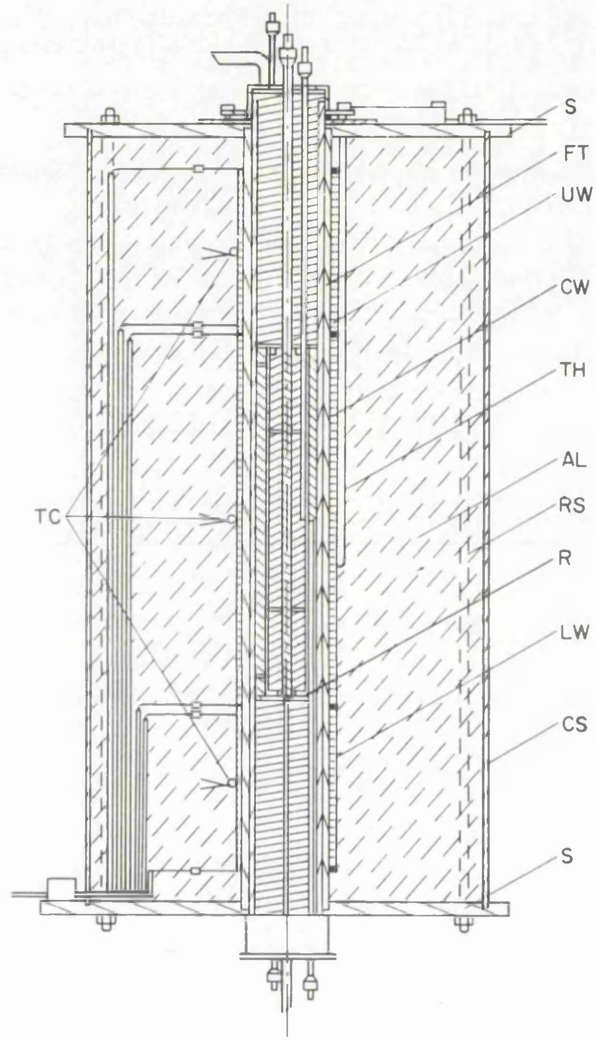

FIG. 2. Thermostat assembly.

Manual control of the end heaters UW, LW is obtained by means of Variacs. The power to the end windings is supplied through a Sorensen voltage regulator. In order to keep a check on the temperature of the windings three quartz insulated chromel–alumel thermocouples TC are located on the surface at the centre of each winding. The furnace tube FT is surrounded by a thick layer of finely grained aluminium oxide powder AL which is contained in a cylindrical copper shell CS. Sindanyo end caps S are placed on the ends and the complete assembly is held together and kept rigidly fixed on the test rig framework by means of four steel rods RS. The complete thermostat is placed in a room where the temperature can be controlled to within $\pm 0{\cdot}5$ degC. The dimensions of the furnace are formulated on the conclusions of Laubitz [3]. The work of Motzfeldt [4] was also consulted.

By careful adjustment of the guard heaters the furnace can be controlled such that the gradient along the length of the test cell area can be no more than a few thousandths of a degree. The temperature stability can be controlled such that the variation in temperature over periods of 30 min–1 h does not exceed 0·02 degC and over periods of 5–10 min is of the order of only a thousandth of a degree.

All electrical measurements which require accurate measurement such as the thermocouple e.m.f's and the power input to the d.c. heater in the centre of the emitter are made with a Diesselhorst pattern thermo-electric free potentiometer. The potentiometer has two ranges 2×10^{-1} V and 2×10^{-2} V. An automatic current controller controls the potentiometer current to one part in 10^6. A photocell galvanometer amplifier provides amplification in the detection circuit. The sensitivity is such that with Pt – Pt – 13% Rh. thermocouples temperature discrimination of $2{\cdot}5 \times 10^{-3}$ °C can be made. To reduce errors due to switching the switches, which utilize thick copper terminals and spring loaded copper switching leaves are completely immersed in heavy gauge copper tanks filled with moisture-free paraffin. So that the effects of thermal e.m.f's in the measuring circuit can be eliminated a thermo-electric free reversing switch is also incorporated in the circuit.

The pressure of the gas is measured utilizing a U-tube mercury manometer. The quartz tube containing the cell is sealed at both ends by means of stainless steel end caps bearing on Viton "O"-rings which are located in "dovetail" grooves at each end of the thermostat. The thermocouple and heater tubes are sealed in a similar manner.

4. EXPERIMENTAL PROCEDURE

The apparatus was filled with the appropriate test gas by allowing the gas to flow through for a period of approximately 30 minutes. The gas inlet and outlet valves were then closed.

The thermostat, which had been previously calibrated, was then switched on. The temperature controller was set to obtain the desired temperature and appropriate adjustments of the guard heater Variacs were made. When stable isothermal conditions were reached the e.m.f's of the thermocouples were intercompared. One thermocouple was chosen as the "standard" thermocouple and the e.m.f's of the other thermocouples compared with this one. When the differences had been noted checks on these values were carried out by quickly interchanging each thermocouple in turn with the "standard" thermocouple and again noting the differences. In making these measurements the reversing switch in the circuit was utilized and readings both "direct" and "reverse" were made. To ensure that the differences were both accurate and consistent this process was repeated several times over a period of several hours. At each temperature over the range 100–300°C at which thermal conductivity determinations were made this procedure was used and plots of the differences against e.m.f. drawn. It was noted that as the temperature at which conductivity determinations were made was increased the differences between the thermocouples increased. At the maximum temperature at which experiments were carried out the differences between the thermocouples were of the order of 0·8 μV. It is considered that the error in the differences found in this way did not exceed 0·1 μV.

The d.c. heater in the centre of the emitter was then switched on in order to establish a suitable temperature difference across the gas annulus. In these experiments various temperature differences were used, varying between 2 and 5 degC. The cell guard heaters were then adjusted so that the temperature difference between the centre of the emitter and each of the guard heaters did not exceed 0·1 μV. When steady state conditions were reached determinations of the apparent thermal conductivity were begun.

Readings of the thermocouple e.m.f's, the voltage drop across the emitter heater and the current passing through the emitter heater were taken at regular intervals over a period of at least 30 min. Readings both "direct" and "reverse" were noted. This procedure was repeated for all temperatures at which thermal conductivity determinations were made.

Over the intervals of time in which steady state readings were taken the variation in mean temperature did not generally exceed 0·02 degC and in many cases was less than 0·01 degC. Over 5–10 min intervals variations were of the order of a few thousandths of a degree. The temperature differences between the thermocouples were constant and only slight variations of the order of one part in 10^3 in the power input to the emitter heater were noted over these 30-min periods. In many cases as an additional check the thermocouples were again interchanged while the apparatus was still at steady state conditions and e.m.f's intercompared. This always confirmed the accuracy of the original intercomparisons.

The argon (99·99 per cent purity) and nitrogen (99·9 per cent purity) used in experiments were supplied directly from commercially available gas cylinders and the apparatus was frequently charged with a new sample of gas. The steam used in the brass cell experiments was supplied from a boiler filled with pure degassed–demineralized water. In these steam experiments all external portions of the apparatus which contained steam had to be kept heated at a temperature of above 100°C in order that the pressure of the steam in the cell could be kept close to atmospheric.

5. CONSIDERATION OF POSSIBLE ERRORS AND CORRECTIONS

The influence of any axial heat flow from the emitter section of the test cell was kept very small in these experiments in three ways. By making the gap between the emitter and heat guards of low conductance, by accurately matching the temperatures of the heat guards with the temperature at the centre of the emitter and by using reasonably large radial heat flows. The influence of axial heat flow, caused by inaccurate matching of the thermocouples was noted at each point at which thermal conductivity determinations were made. However in order to make a more accurate assessment of this influence a series of tests were carried out at a temperature of 211°C. The heat input to the emitter section was kept constant and the heat inputs to the guard heaters adjusted so that the cell temperatures were out of balance. The influence of this out of balance on the measured value of the thermal conductivity of the test gas was noted. This was done for several different degrees of out of balance and a plot of measured conductivity against out of balance was drawn. These experiments showed that the maximum possible error caused by axial heat flow in the thermal conductivity determinations could be estimated to be less than 1 per cent.

The influence of thermal radiation was small due to the low emissivity of the test cell material and the very narrow annulus used. Calculation showed that the maximum influence at the highest temperature was some 0·3 per cent. For nitrogen and argon the effect was estimated utilizing the well known equation:

$$q_{r\ \text{transparent}} = \frac{\sigma 2\pi r_1 L(T_1^4 - T_2^4)}{\dfrac{1}{\epsilon} + \dfrac{r_1}{r_2}\left(\dfrac{1}{\epsilon} - 1\right)}.$$

Utilization of the above equation for an emitting and absorbing medium, such as steam, is not accurate and is permissible only when the radiation effect is smaller than the experimental error of the conductivity determinations. The problem of combined conduction and radiation in an emitting and absorbing medium has been studied by Leidenfrost [18] and as stated in his paper a more accurate though more complex correction must be used if serious errors in conductivity determinations are to be avoided particularly at high temperatures. It has been shown by Kraussold [17] among others that when the Grashof–Prandtl product is less than 1000 the influence of convection effects on the thermal conductivity determinations is very small. In these experiments convection effects were negligibly small.

Calibration of the thermocouples, which conform with the British Standard Institute's Tables B.S. 1826, showed that the error in overall temperature was only some 0·1 per cent. The fact that the thermocouples were located slightly below the cell surfaces was taken into account. Calculation showed that any small temperature differences which existed between the points at which the temperatures were measured and the cell surfaces during conductivity determinations were very small, maximum influence some 0·3 per cent. Calculation also showed that since the pressure of the gas was atmospheric and the temperature at which determinations were made were only moderately high corrections for "thermal jump" effects were small.

Corrections had to be applied to the cell constant, which was measured at 20°C, to compensate for the expansion of the cell with temperature. When assembling the cell concentricity of the emitter inside the receiver was checked by means of a calibrated wire such that the maximum eccentricity could be some 0·0002 in. Calculations showed that an error caused by this eccentricity was negligible.

When all factors are considered the probable accuracy of the presented data can be estimated to be within $\pm 1{\cdot}5$ per cent.

Table 2. Results

point number	(A) Silver cell temperature (°C)	$\lambda \times 10^5$ (W/cm °K)
(a) Argon		
(1)a	152·7	23·5
(2)a	156·4	23·5
(3)a	174·7	24·6
(4)a	175·3	24·5
(5)a	175·9	24·4
(6)a	212·0	25·4
(7)a	212·1	25·8
(8)a	212·4	25·3
(9)a	248·5	27·4
(10)a	249·4	27·7
(11)a	249·5	27·3
(12)a	279·2	27·8
(13)a	279·7	28·0
(14)a	280·0	28·0
(b) Nitrogen		
(15)a	154·2	33·9
(16)a	172·4	35·8
(17)a	173·7	35·8
(18)a	211·4	37·3
(19)a	211·7	37·2
(20)a	248·0	39·9
(21)a	248·0	39·6
(22)a	248·0	38·8
(23)a	278·3	41·3
(24)a	278·8	41·2
(25)a	279·5	40·9

point number	(B) Brass cell temperature (°C)	$\lambda \times 10^5$ (W/cm °K)
(a) Argon		
(1)b	145·9	23·0
(2)b	149·8	22·8
(3)b	166·9	24·0
(4)b	170·8	23·9
(b) Nitrogen		
(5)b	146·4	33·5
(6)b	148·4	34·1
(7)b	168·2	35·0

point number	(C) Steam temperature (°C)	$\lambda \times 10^5$ (W/cm °K)
(8)b	142·4	27·8
(9)b	143·8	28·5
(10)b	158·6	29·3

6. RESULTS

The values obtained are shown in Table 2. Each value quoted is the result of at least seven separate determinations. Figures 3–5 show the values obtained in this work along with the recent correlations of Vargaftik and Zimina [5–7]. Also shown are some of the more recent determinations of other workers. For argon and nitrogen, Vines [2], Nuttall and Ginnings [8], Johannin and Vodar [9], Geier and Schafer [10], Schottky [11], Zaitseva [12], Keyes and Vines [13]. For steam the values

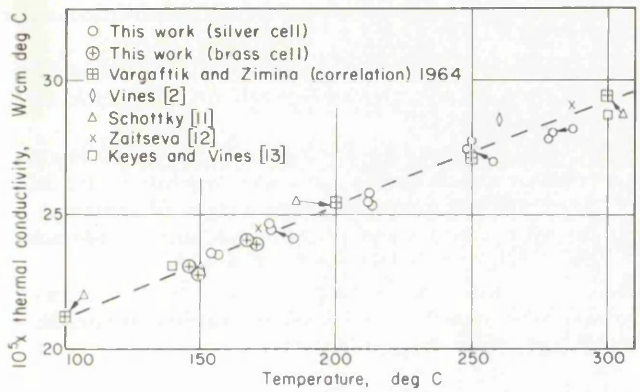

FIG. 3. Thermal conductivity of argon against temperature pressure: 1 atmosphere.

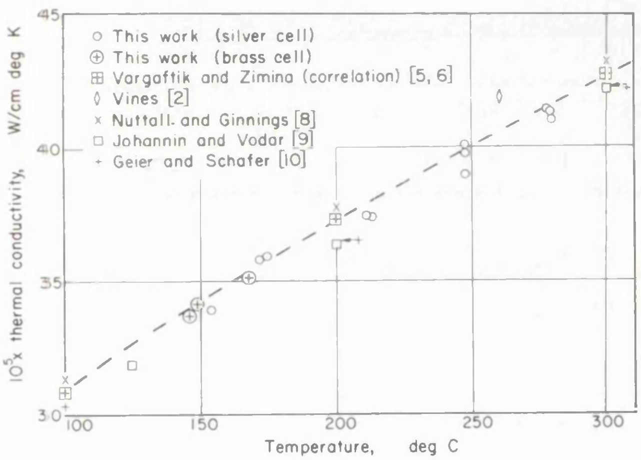

FIG. 4. Thermal conductivity of nitrogen against temperature pressure: 1 atmosphere.

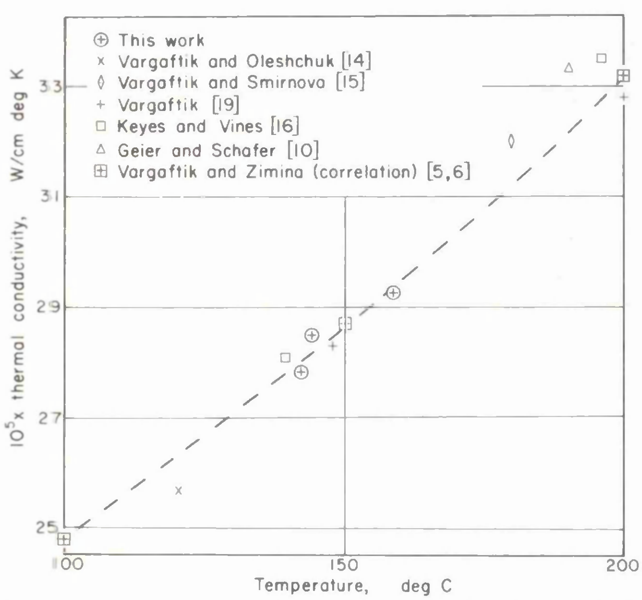

FIG. 5. Thermal conductivity of steam against temperature pressure: 1 atmosphere.

shown are those of Vargaftik and Oleshchuk [14], Vargaftik and Smirnova [15], Vargaftik [19], Keyes and Vines [16], Geier and Schafer [10] and Vargaftik and Zimina [5].

7. CONCLUSIONS

The results obtained show good agreement with the results of other workers in this region. The mean deviation of the points from the correlations of Vargaftik and Zimina is some 1 per cent. The results confirm the accuracy of the test rig.

ACKNOWLEDGEMENTS

This work was carried out at the Mechanical Engineering Research Annexe of the University of Glasgow as part of a current series of investigations on thermodynamic and transport properties of steam now being undertaken at this laboratory and sponsored by the Central Electricity Generating Board and the South of Scotland Electricity Board.

The author would like to acknowledge the assistance given to him by Dr. E. A. Bruges who supervised this work.

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Résumé—On décrit ici les mesures du coefficient de conductibilité thermique de l'argon et de l'azote dans la gamme de 100 à 300°C à la pression atmosphérique en employant une cellule à cylindres concentriques en argent munie de cylindres de garde.

On donne aussi les résultats pour l'argon, l'azote et la vapeur d'eau dans la gamme de 140 à 180°C à la pression atmosphérique en employant une cellule à cylindres concentriques en laiton.

Les résultats sont en bon accord avec les valeurs publiées récemment. La déviation moyenne des points à partir des relations publiées récemment, pour ce gaz, par Vargaftik et Zimina est d'environ de 1 pour cent.

Zusammenfassung—Es werden experimentelle Lösungen beschrieben für die Wärmeleitfähigkeit von Argon und Stickstoff im Bereich 100–300°C, bei Atmosphärendruck, wobei eine Zelle aus konzentrischen Silberzylindern verwendet wurde.

Ausserdem sind Ergebnisse für Argon, Stickstoff und Dampf im Bereich 140–180°C und Atmosphärendruck angegeben, die in einer Anordnung konzentrischer Zylinder aus Messing erhalten wurden.

Die Ergebnisse zeigen gute Übereinstimmung mit kürzlich veröffentlichten Werten. Die mittlere Abweichung von Punkten nach einer neueren Korrelation für diese Gase nach Vargaftik und Zimina betragen etwa 1 %.

Аннотация—В данной статье описывается экспериментальное измерение коэффициента теплопроводности аргона и азота в диапазоне 100–300°С при атмосферном давлении путем использования серебряной концентрической цилиндрической ячейки.

Также приводятся результаты по аргону, азоту и пару в диапазоне 140–180°С при атмосферном давлении, полученные с помощью латунной концентрической цилиндрической ячейки.

Результаты хорошо согласуются с недавно опубликованными. Для данных газов среднее отклонение точек от недавно опубликованных данных Варгафтика и Зимина оставляет около 1%.

APPENDIX (B)

Appendix (B)

A New Concentric Cylinder Thermal Conductivity Cell

Summary

A new thermal conductivity cell utilising an emitter constructed of an anisotropic material, pyrolytic graphite, for measurements in the temperature range 0°C - 100°C at atmospheric pressure is described. The test fluid fills an annulus 0.5 mm wide between concentric cylinders. By measuring the power dissipated in the measurement section of the inner cylinder and the temperature difference across the fluid annulus determination of the thermal conductivity of the test fluid can be made.

Preliminary measurements, believed accurate to ± 2%, on nitrogen for the temperature range 30°C - 80°C, along with one determination for argon and one determination for air are given.

(1) Introduction

For accurate measurement of the coefficient of thermal conductivity for both gases and liquids a steady state method utilising a vertical concentric cylinder cell with two guard heaters has been widely used. Such experimenters as Vines (1), Venart (2) and Vargaftik and Smirnova (3) have utilised cells of this construction for conductivity measurements performed at atmospheric pressure.

Since cells of this geometry give a close approximation to infinite coaxial cylinders the Fourier equation

$$\lambda = \frac{q \log_e {}^{r}2/r_1}{2\pi L(T_1 - T_2)} \quad ......(1)$$

(where λ = the thermal conductivity of the test fluid, q = the heat transmitted from the measurement section of the emitter, r_2 = the internal radius of the outer cylinder, r_1 = the radius of the inner cylinder, T_1 and T_2 = the temperatures of the inner and outer cylinders respectively and L = the length of the measurement section) may be used.

So that equation (1) may be used with a high degree of accuracy previous experimenters have shown how axial heat flow may be reduced to a very small value by:-

(a) Making the ratio of emitter length to diameter large

(b) Making the heat guard gaps of low conductance

(c) Accurately matching the temperature of the heat guards with the temperature of the emitter

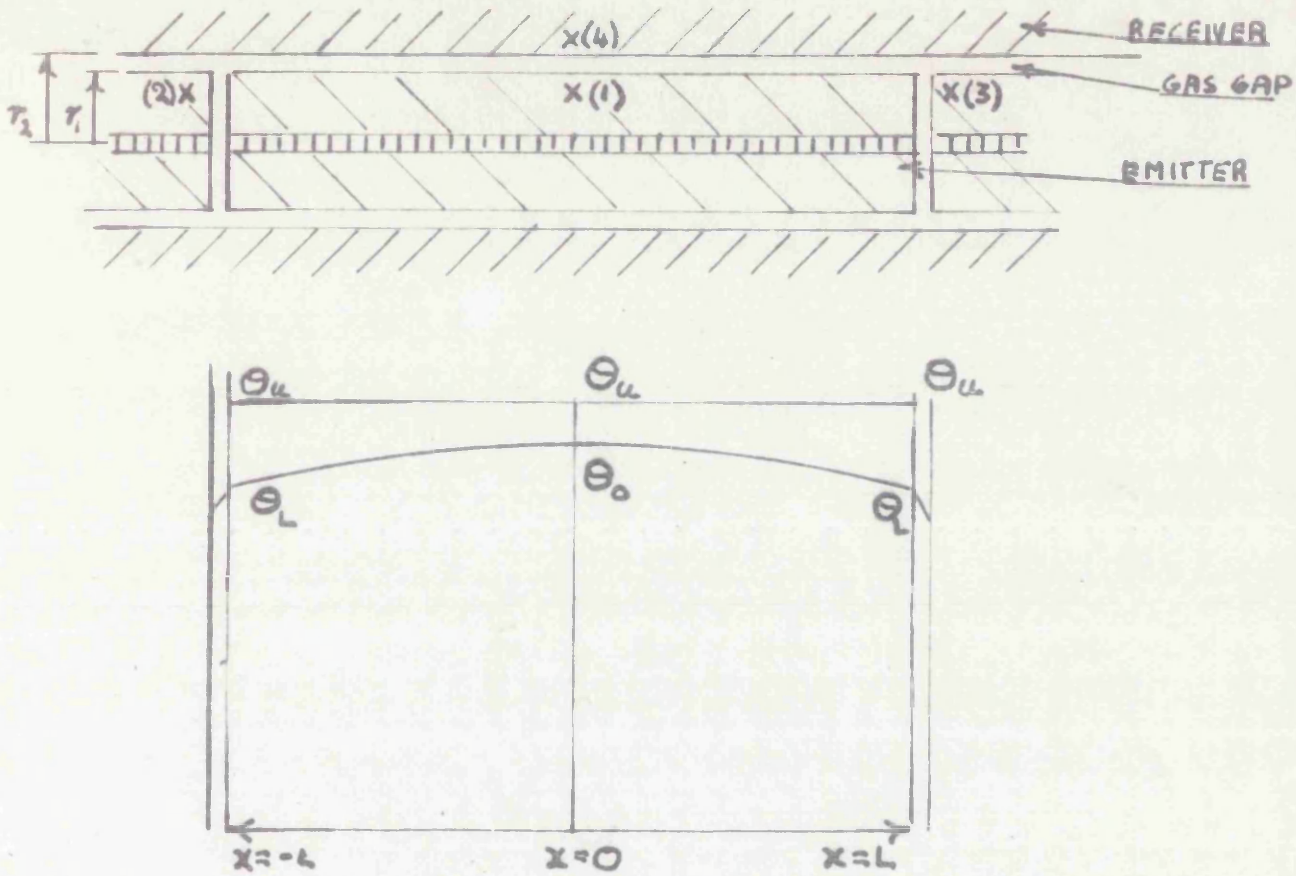
(d) Using large heat inputs to the emitter measurement section heater.

In taking these precautions difficult problems are encountered. If the emitter length to diameter ratio is made large the cell length is rather long or a thin somewhat fragile cell of small diameter must be used. The long, thick cell emitter is preferable because of its mechanical rigidity. In using such a cell, however, problems in thermostat design increase since it is difficult to obtain satisfactory isothermal conditions along the length of the cell. It should also be noted that, since for various experimental reasons the annulus width separating the emitter and the receiver must be made very small, the cell cylinders must be very accurately machined and finished if errors in thermal conductivity determinations are to be avoided. The difficulties in manufacturing a cell to the close tolerances required are considerably increased when the cell is long and are even more troublesome when the cell is thin and not very rigid.

It is also true, as has been stressed by Leidenfrost (5) that accurate control of the cell guard heaters considerably increases the time necessary to obtain conductivity measurements.

The use of a large heat input to the emitter measurement section is often not desirable. Apart from the problems of designing a small heater powerful enough, large heat inputs can lead to difficulties in maintaining accurate thermostat temperature control (as was noted by Venart (4) in his work, on measuring the thermal conductivity of water) and also convection problems can arise in certain cases. In addition if the temperature of the emitter is considerably higher than the temperature of surrounding material then large axial gradients will exist between the outer ends of the heat guards and surrounding material. Large gradients along the thermocouple and heater tubes and wires can cause serious errors in measured temperatures and heat inputs.

In addition to the main project undertaken by the author, which was to measure the thermal conductivity of steam in the range $100^{\circ}C - 700^{\circ}C$ at atmospheric pressure, some additional time was spent in investigating how the use of the anisotropic material, pyrolytic graphite, in a cylindrical conductivity cell, might help reduce these noted difficulties.



INFLUENCE OF AXIAL HEAT FLOW

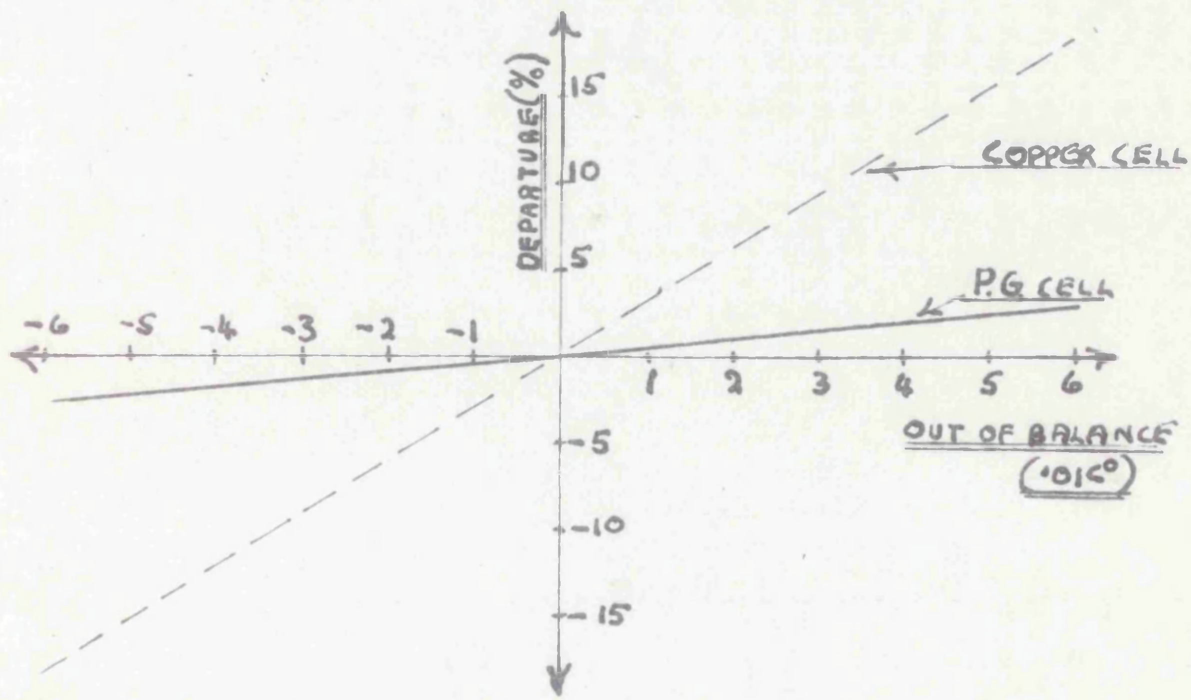


FIGURE B(1)

HEAT INPUT = 0·25 WATTS

MEAN TEMPERATURE = 33°C

(2) Pyrolytic Graphite

Pyrolytic graphite is a graphite formed from a pyrolytic deposition process. In this process pure carbon atoms are deposited layer by layer on a suitably prepared substrate. Material formed in this way is spectroscopically pure carbon and it is free of voids.

As a result of this process certain properties measured parallel to a surface differ greatly from values measured perpendicular to the surface. For the range of temperatures in which thermal conductivity measurements, using a graphite emitter, were made the ratio of the thermal conductivity in the axial direction of the emitter to thermal conductivity in the radial direction is less than 0.01. The thermal conductivity in the radial direction has a similar value to that of silver and copper. The properties of the material were obtained from reference (6).

The main disadvantage of using this material in a conductivity cell are the high emissivity of the material and the fact that at present it can only be obtained in blocks of maximum thickness equal to $\frac{3}{4}$".

(3) Advantage of This Cell

The problem of calculating the effect of axial heat flow in the cylindrical heating element of a thermal conductivity cell has been tackled by Jacob (7) for an emitter with an equal out of balance in temperature at each end. If heat flow from the emitter was strictly radial then (see figure B(1)) ignoring any radial temperature drop in the cell material

$$\frac{q}{2L} = \frac{\lambda_{GAS}\, 2\pi\, \theta_u}{\log_e \frac{r_2}{r_1}} \qquad \ldots\ldots (2)$$

(where q = total heat input to the emitter, λ gas = thermal conductivity of the test gas, θ_u = radial temperature difference between emitter and receiver, r_1 = the radius of the emitter and r_2 = the internal radius of the receiver, $2L$ = the emitter length).

If some of the heat in the emitter flows axially then equation (2) may be replaced by (assuming receiver isothermal)

$$\frac{d^2\theta}{dx^2} = m_a^2\,\theta - \frac{q}{2L(\lambda A)_a} \qquad \ldots\ldots (3)$$

(where θ = temperature difference across the gas gap at a distance x from the centre of the emitter, and $m_a = \sqrt{\dfrac{\lambda_{GAS}\, 2\pi}{(\lambda A)_a \log_e \frac{r_2}{r_1}}}$ where $(\lambda A)_a$ = axial conductance of emitter).

The solution to this equation may be written as

$$\theta - \theta_0 = 2\left(\theta_0 - \frac{q}{2L(\lambda A)_a m_a^2}\right)\left(\sinh \frac{m_a x}{2}\right)^2 \ldots\ldots (4)$$

(where θ_0 = the temperature difference across gas annulus at $x = 0$)

From equations (2) and (4) Jacob has shown that

$$\theta_u = \frac{\theta_o \cosh(m_a L) - \theta_L}{\cosh(m_a L) - 1} \quad \ldots (5)$$

(where θ_L = temperature difference across gas annulus at $x = -L$ and $x = L$)

From equation (3)

$$\frac{d^2\theta}{dx^2} = C_1\theta - C_2$$

$$\therefore \quad 2\frac{d\theta}{dx}\cdot\frac{d^2\theta}{dx^2} = 2C_1\theta\frac{d\theta}{dx} - 2C_2\frac{d\theta}{dx}$$

integrating

$$\left(\frac{d\theta}{dx}\right)^2 = C_1\theta^2 - 2C_2\theta + K$$

(where K = constant)

at $x = 0$, $\frac{d\theta}{dx} = 0$, $\theta = \theta_o$ $\therefore$ $C_1\theta_o^2 - 2C_2\theta_o + K = 0$

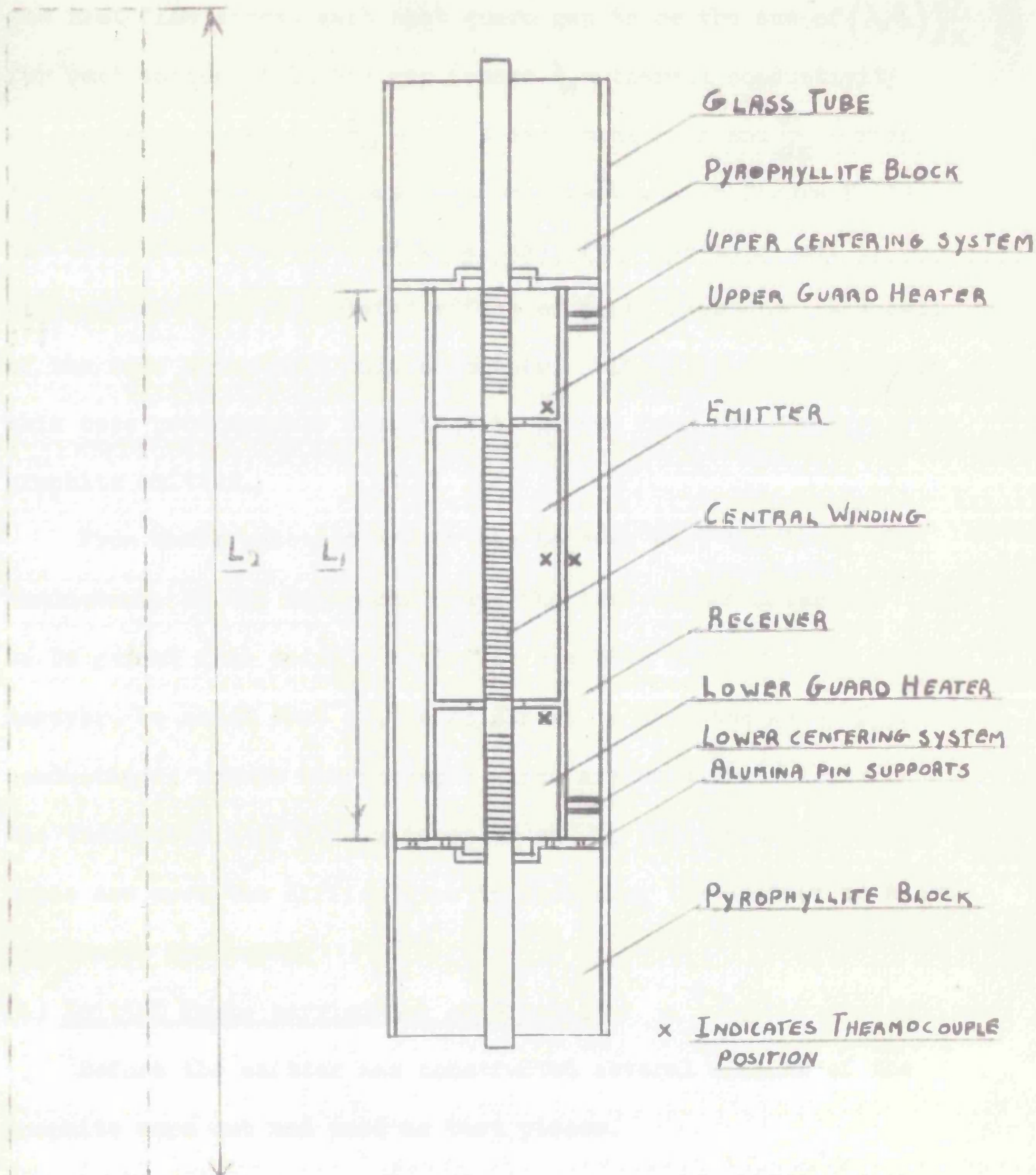
at $x = L$, $\frac{d\theta}{dx} = \left(\frac{d\theta}{dx}\right)_{x=L}$, $\theta = \theta_L$ $\therefore$ $C_1\theta_L^2 - 2C_2\theta_L + K = \left(\frac{d\theta}{dx}\right)^2_{x=L}$

subtracting

$$\left(\frac{d\theta}{dx}\right)^2_{x=L} = \frac{2q}{2L(\lambda A)_a}(\theta_o - \theta_L) - \frac{\lambda_{GAS}\,2\pi}{(\lambda A)_a \log_e \frac{r_2}{r_1}}(\theta_o + \theta_L)(\theta_o - \theta_L) \ldots\ldots (6)$$

Assuming the temperature distribution in the cell to be similar to that shown in figure B (1) the effects of axial heat flow for this cell may be estimated from temperatures measured at points (1), (2), (3) and (4). Knowing approximately the conductivity of the test gas, the test cell material and the conductivities of the various materials which the various com-

THERMAL CONDUCTIVITY CELL



OUTLINE OF VENART'S EMITTER

FIGURE B (2)

ponents (thermocouple and heater tubes, wires etc.) are made, as well as the component dimensions, the influence of axial heat flow may be estimated using equations (2), (5) and (6) and estimating the heat flow across each heat guard gap to be the sum of $(\lambda_n A_n)\frac{dT}{dx}$ for each component in the gap (where λ_n = thermal conductivity of component material, A_n = cross sectional area and $\frac{dT}{dx}$ = mean temperature gradient across each component). In figure B (1) the calculated influence of axial heat flow for this cell is compared with the calculated effect of axial heat flow in a cell of the same dimensions made of copper. It will be seen that in this case considerable advantage is gained from using a pyrolytic graphite emitter.

From these calculations it can be seen that the lower the conductance of the heat guard gaps the less is the advantage to be gained from using a pyrolytic graphite emitter. It should, however, be noted that if, in an effort to keep the gaps of low conductance, narrow thermocouple wires are used instability in the thermocouple is likely to occur and if thin emitter support tubes are used the difficulties in machining the emitter to exact tolerances increases.

(4) Initial Tests carried out on Graphite

Before the emitter was constructed several samples of the graphite were cut and used as test pieces.

Initial tests were carried out on the machinability of the material. After machining several small cylinders it was

CIRCUIT FOR THERMOSTAT WATER CIRCULATION

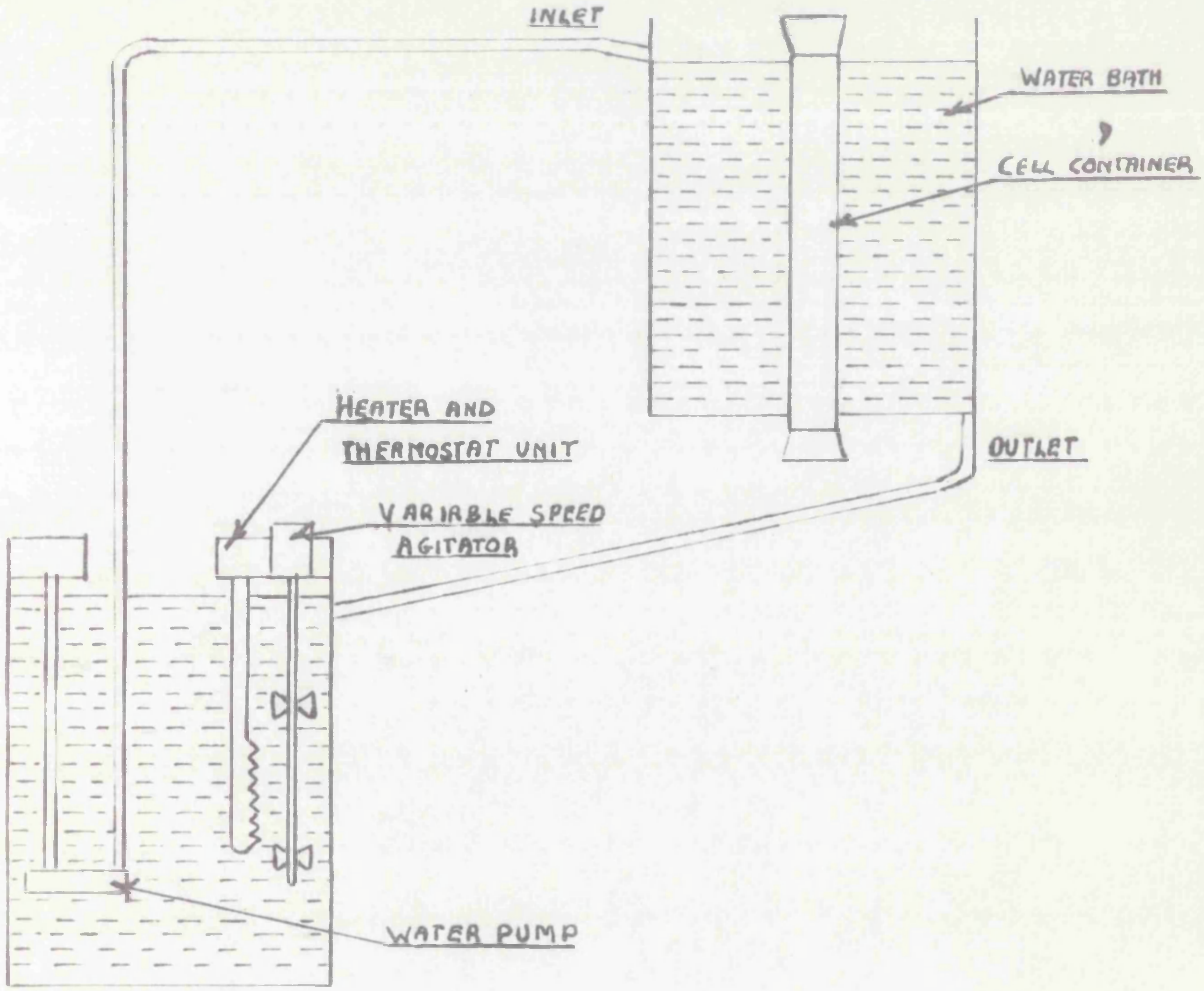


FIGURE B(3)

confirmed that it could be machined to the close tolerances required for a thermal conductivity cell and that a very smooth surface finish could be obtained.

Tests were carried out to join several blocks together with a graphite cement. This was quite successful but led to additional problems in the final machining of the cell components. Since the blocks in which the graphite is supplied are extremely flat it was noted that, when several blocks were mounted on a central rod and held together by means of nuts on each end of the rod, an excellent smooth continuous cylindrical surface could be machined.

Since the high emissivity of the surface makes the material unsuitable foruse in a high temperature conductivity cell several attempts were made to coat the surface of some samples with a thin metal film. All attempts proved unsatisfactory.

(5) Description of Apparatus

A drawing of the cell is shown in figure B (2). The cell consists of an emitter and a receiver. The cylindrical emitter and two guard cylinders, made of pyrolytic graphite, are mounted on a slim stainless steel tube and held together by means of nuts on each end. The gaps separating the guard cylinders from the measurement section are 1 mm (approximately). Surrounding the emitter is the copper receiver. The emitter is located coaxially by means of six screws bearing on slim mica spacers (slightly less than the gap size in thickness) three spaced at 120° intervals around near the top and three spaced similarly near the bottom. The centering devices are located well away from the measuring section.

The emitter heater consists of a 6 bore 1.8 mm diameter alumina tube onto which the measurement section and guard heater windings are spaced and cemented in position. The windings are made from 41 s.w.g. michrome wire. Copper current leads (32 s.w.g.) are silver soldered to the ends of the measurement section heater. The assembly is enclosed in a thin-walled stainless steel tube which fits closely into the heater pocket.

The thermocouples used were made from 32 s.w.g. copper, constantan wires. The wires were supported in slim 2 bore 1.2 mm diameter alumina tubes which fitted neatly into the thermocouple wells provided. An ice bath provided zero reference temperature.

All electrical measurements which need be known accurately were made with a Diesselhorst pattern thermo-electric free potentiometer. All necessary precautions were taken to eliminate spurious e.m.f.s.

The complete conductivity cell was mounted vertically in a glass tube sealed at both ends with rubber end caps. The spaces between the cell ends and the ends of the glass tube were filled with pyrophyllite blocks.

The glass tube was placed in a thermostated water bath (see figure B (3)). The temperature of the water was maintained by the use of a heater and a thermostat unit. To prevent non-uniform temperature regions the fluid was circulated at a high velocity by a water pump. The bath temperature could be controlled to better than $\pm$ 0.05 C^{o} in the temperature range 30^{o}C - 80^{o}C.

Gas inlet and outlet valves were positioned at the bottom and top of the glass tube respectively and the cell could be flushed out with a fresh charge of gas when it was thought desirable.

(6) Experimental Procedure

In calibrating the thermocouples one was chosen as a 'standard' and was calibrated in the range 30^{o}C - 80^{o}C against a N.P.L. calibrated platinum resistance thermometer. The calibration curve obtained fitted an equation of the form $e = at + bt^2 + dt^3$ (where e = emf, t = temperature(^{o}C) and a,b and c are constants) with a maximum deviation of 1 μV. Calibration of the other thermocouples was performed by differencing them from the 'standard' thermocouple. The differences found did not exceed $\pm$ 1 μV.

The procedure for obtaining each of the conductivity values was as follows. The bath temperature was first controlled at the desired temperature for approximately one hour. The emitter central heater was then switched on to establish a temperature difference across the gas annulus. Temperature differences used were between 2 C^{o} and 7 C^{o}. The guard heaters were then switched on and appropriate adjustments made. When stable conditions were achieved, measurement of the temperature difference and central heater current and voltage were made. Thermal conductivity values could then be calculated using equation (1).

(7) Consideration of possible errors and corrections

A volt ratio box was placed in parallel with the emitter heater so that the voltage across the heater could be determined by use of the potentiometer. Corrections had to be applied to take into account the small current which flowed through the box during steady state thermal conductivity determinations. This correction amounted to some 0.4% of the total heat input in all cases. Convection effects were calculated to be negligible. Calculation also showed that radiation accounted for some 0.3% - 0.4% of the total heat input, depending on temperature. The calculated influence of axial heat flow plotted in figure B (1) showed that for a temperature out of balance of .02 C$^{\circ}$ at a heat input of 0.25 watts the error in measured conductivity would be some 1%. Since heat inputs of 0.5 - 0.7 watts were generally used and the cell could readily be balanced to within .02 C$^{\circ}$ the influence of axial heat flow on conductivity determinations was calculated to be less than 0.5% in most cases.

The temperature drop in the cell material was so amall that calculation showed it could be neglected and temperature discontinuity effects at the cell surfaces were also calculated to be negligible.

The cell constant was calculated from measurement of the cell length and emitter and receiver radii (given in Table (1)) and the possible errors in these values taken into account. The cell constant was adjusted for each temperature at which conductivity determinations were made to allow for thermal expansion of the cell components and possible eccentricity effects taken into account.

The nitrogen (99.9% purity) and argon (99.99% purity) were supplied directly from commercially available gas cylinders.

(8) Results

The results obtained are shown in figure B (4) and compared with recent correlated values for these gases given by the Thermophysical Properties Research Centre (8) and the U.S. National Bureau of Standards (9). The value obtained for air agrees well with the T.P.R.C. correlation. The nitrogen values show excellent agreement with the values of Johannin and Vodar(10). However, these points and the argon point suggest values some 2.5% lower than those recommended.

(9) Conclusions

The use of pyrolytic graphite to form a short yet thick emitter substantially reduces the difficulties in machining the cell components mentioned in section (1). (A comparison of the dimensions of Venart's emitter (reference (2)) with the emitter of the present cell is shown in figure B (2)). A small compact thermostat was used. The heat input to the cell guard heaters could easily be adjusted such that even for very small heat inputs to the emitter the influence of axial heat flow on conductivity determinations was very small.

The thermal conductivity values obtained from this preliminary investigation serve to indicate that the cell can be used to obtain accurate values. An evaluation of all the variables involved in this experimental work indicates that the error in the values of thermal conductivity obtained can be estimated to be within $\pm$ 2%.

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TABLE I

CELL DIMENSIONS

Diameter of Emitter = 1.7348 centimetres $\pm$.003 centimetres.

Diameter of Receiver = 1.8372 centimetres $\pm$.0003 centimetres.

Length of Measurement Section = 3.81 centimetres $\pm$.001 centimetres

Total length of Cell = 7.62 centimetres.

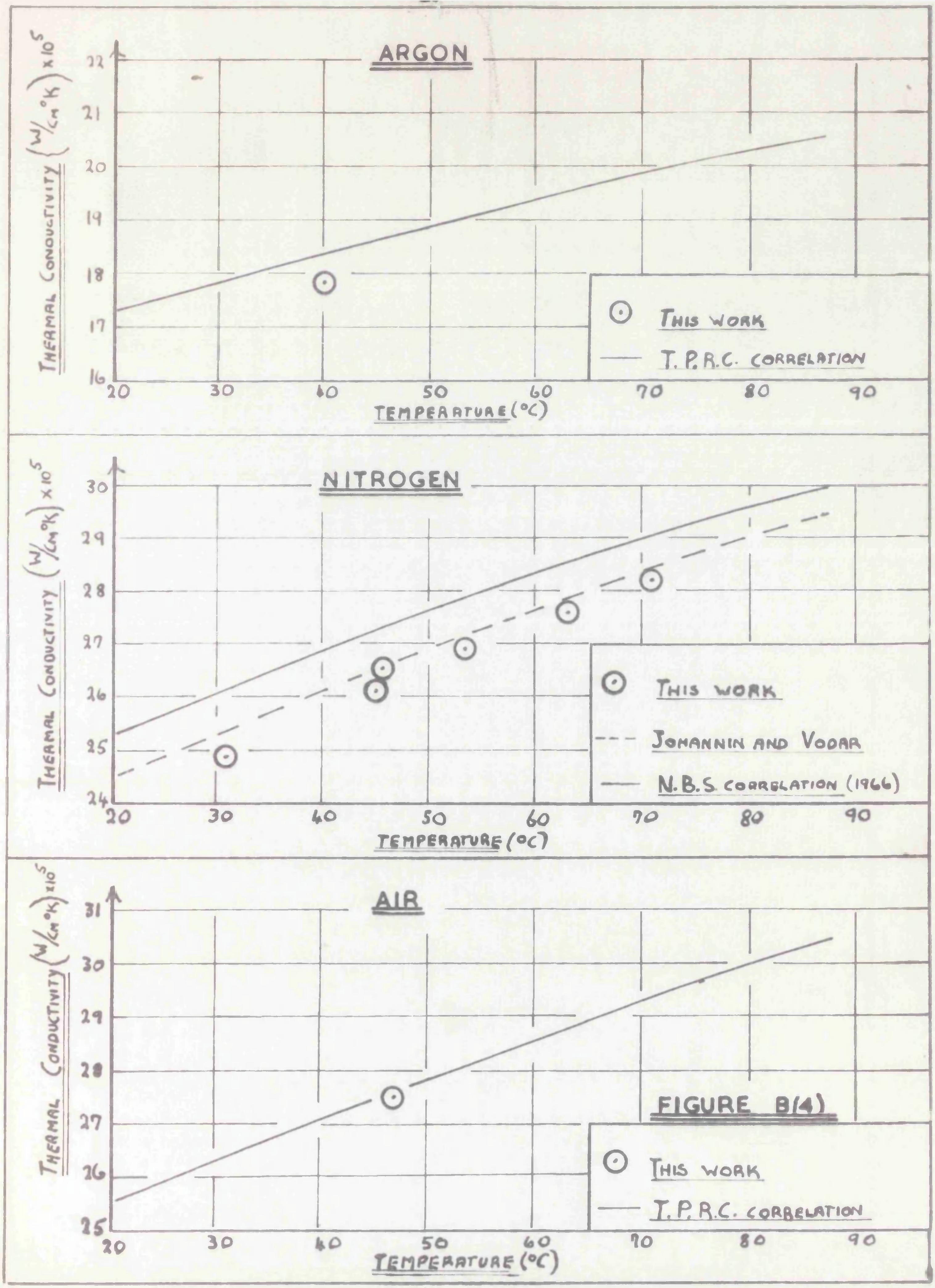
ARGON
THERMAL CONDUCTIVITY (W/CM °K) x 10^5
TEMPERATURE (°C)
THIS WORK
T.P.R.C. CORRELATION
NITROGEN
THERMAL CONDUCTIVITY (W/CM °K) x 10^5
TEMPERATURE (°C)
THIS WORK
JOHANNIN AND VODAR
N.B.S CORRELATION (1966)
AIR
THERMAL CONDUCTIVITY (W/CM °K) x 10^5
TEMPERATURE (°C)
THIS WORK
T.P.R.C. CORRELATION

FIGURE B(4)