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NEW THERMAL CONDUCTIVITY MEASUREMENTS FOR ARGON, NITROGEN AND STEAM

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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

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

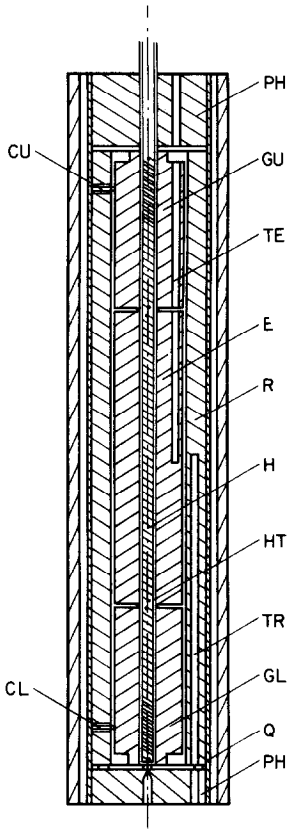

FIG. 1. Thermal conductivity cell.

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.

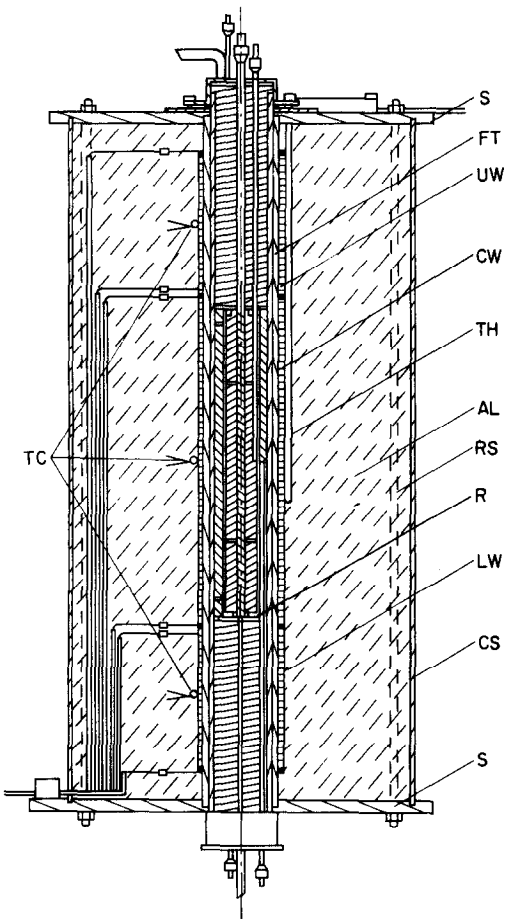

FIG. 2. Thermostat assembly.

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 determina-

tions 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:

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

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.

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

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

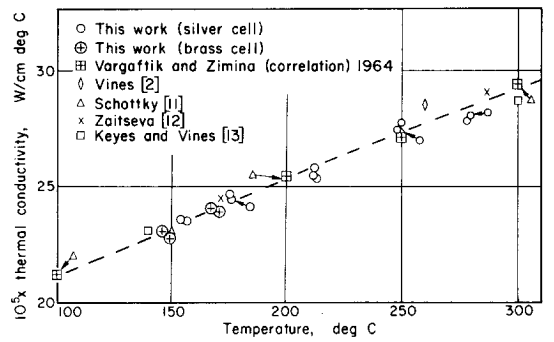

FIG. 3. Thermal conductivity of argon against temperature pressure: 1 atmosphere.

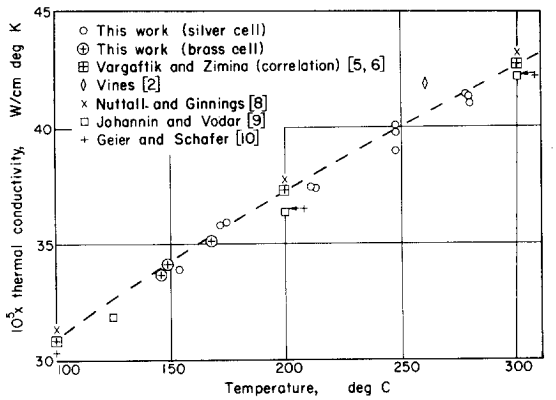

FIG. 4. Thermal conductivity of nitrogen against temperature pressure: 1 atmosphere.

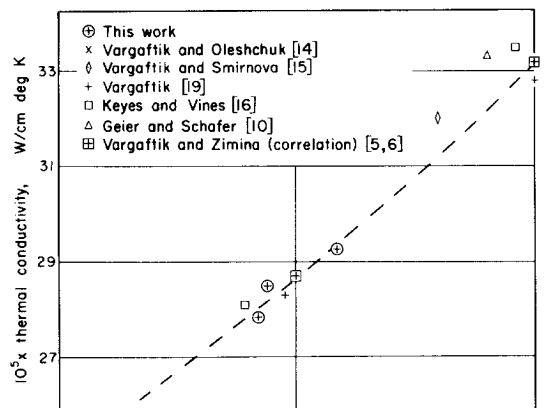

FIG. 5. Thermal conductivity of steam against temperature pressure: 1 atmosphere.

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

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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°C при атмосферном давлении путем использования серебряной концентрической цилиндрической ячейки.

Также приводятся результаты по аргону, азоту и пару в диапазоне 140–180°C 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%.