MEASUREMENT OF THERMAL CONDUCTIVITY OF GASES USING THERMAL DIFFUSION COLUMN : NEON

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(*Received April* 14, 1966; *Resubmitted June* 4, 1966)

ABSTRACT. A hot-wire type of thermal diffusion column is employed to measure thermal conductivity of gases. Measurements on neon are reported in the temperature range 323-723°K and for five different values of pressure smaller than an atmosphere. The values agree amongst themselves within a scatter of about 5 per cent and still better with the other existing literature values obtained from established conventional techniques. The success obtained is particularly gratifying when the prospect of thermal conductivity measurements at higher temperatures is recalled

INTRODUCTION

Measurements on thermal conductivity of gases and particularly at high temperatures are of great importance to scientists as well as engineers. For the proper understanding of the exchange of energy between external and internal degrees of freedom of polyatomic molecules such an information is basic. A variety of design engineers also very frequently and in an important way need such values.

It has long been known that reliable and accurate measurement of thermal conductivity of gases is probably the most difficult amongst all the transport properties. This is because many complicated corrections are to be considered and the job becomes increasingly difficult as the temperature of measurement is increased. Purely on the grounds of need in the recent years several very impressive efforts have been made for measuring thermal conductivity at high temperatures. Here we report a part of our continuing effort to determine thermal conductivity using thermal diffusion columns.

The use of columns for thermal conductivity measurements was first suggested and employed by Blais and Mann (1960), who reported results on helium and hydrogen in the temperature range 1200-2000°K. The accuracy of these data is doubtful and it is believed that their values are systematically greater than the actual values, Saxena and Agrawal (1961). A few more arguments in favour of this possibility have been advanced by Saksena (1965). In this laboratory we have revived this work and very encouraging preliminary measurements have been reported on helium and air, Saksena (1965). He employed a system of two glass columns completely identical except for length and measured the thermal conductivity in the temperature range 313–413°K. Differential measurements were taken to avoid the probable losses due to end conduction and these were also theoretically calculated and found to be always less than 0.6 per cent for air and still smaller for helium. These measurements conclusively established the technique in this temperature range because these values were found to be in good agreement with the directly measured values by the conventional thick wire variant of the hot-wire cell, Gambhir (1965) Encouraged by the success of the results obtained we have launched a full range programme to measure thermal conductivity of various pure gases as a function of temperature. This effort has to be preceded by carefully planned sets of crucial runs which may unambiguously establish the technique and provide a clear idea about the precision of measurements In the present article we report the measurements on neon in the temperature range 323–723°K at five different pressures and compare with the existing data obtained from conventional techniques.

THEORY

We now present a brief and relevant account of the theory of this method as particularly applicable to our apparatus design. Assuming the wire to be at a uniform temperature, its ends to be at the same temperature as the cold wall, convection to be absent and the heat flow to be radial, we can write the differential equation giving the heat flow as :

$$\pi a^2 K \frac{d^2\theta}{dz^2} - 2\pi a h_c \theta - Q_r + \frac{I^2 \rho_0 (1+\alpha\theta)}{J} = 0. \qquad \dots \quad (1)$$

Here K stands for the thermal conductivity of the material of the hot wire of radius a at a temperature θ above the cold wall temperature. The wire material has a temperature coefficient of resistance α and ρ_0 is its resistance per unit length at $\theta = 0$. I represents the current through the hot wire and J the mechanical equivalent of heat h_c stands for the loss of heat from the wire per unit area per unit temperature difference by conduction through the gas. Similarly Q_r represents the quantity of heat radiated from a unit length of the wire.

If the column is highly evacuated so that $h_c = 0$, eq. (1) reduces to

$$\pi a^2 K \frac{d^2\theta}{dz^2} - Q_r + \frac{I'^2 \rho_0 (1+\alpha\theta)}{J} = 0. \qquad \dots \quad (2)$$

Here I' represents that value of the current which maintains a particular element of the hot wire to be at the same temperature in vacuum as a current I flowing through it does in the presence of the gas.

Subtracting eq. (2) from (1) we get for the power conducted through the gas

$$2\pi a h_c \theta = \frac{(I^2 - I'^2)\ \rho_0 (1+\alpha\theta)}{J}, \qquad \dots \quad (3)$$

$$\equiv w_e.$$

Now two more reasonable assumptions get associated with equation (3). These are : (a) The temperature distribution along the length of the wire remains practically unchanged with or without the gas, (b) the heat lost by radiation is independent of the nature of surroundings. For a sufficiently long wire the lengths at the two ends where the temperature may be appreciably different from the uniform temperature in the mid region will be relatively small and the first assumption will be reasonable The second assumption is also valid as under normal operating conditions the gas in the column is invariably transparent to thermal radiations. We therefore get for cylindrical geometry and radial heat flow conditions

$$2\pi a h_c \theta = -2\pi a \lambda \left(\frac{d\theta}{dr}\right)$$

$$= \frac{2\pi\lambda}{ln(b/a)}\,\theta. \qquad \ldots \quad (4)$$

Here λ is the thermal conductivity of the gas at the wire temperature and b is the radius of the cold wall. We have consequently,

$$w_c = \frac{2\pi\lambda}{ln(b/a)}\,\theta. \qquad \ldots \quad (5)$$

The eq. (5) leads to

$$\left(\frac{d\omega_c}{d\theta}\right)_{r=a} = \frac{2\pi\lambda}{\ln(b/a)}, \qquad \ldots \quad (6)$$

and alternatively

$$\lambda = \frac{ln(b/a)}{2\pi}\left(\frac{d\omega_c}{d\theta}\right)_r \qquad (7)$$

EXPERIMENTAL

The principal component of our experimental assembly consisted of a conventional hot wire type thermal diffusion column. In principle it consists of a precision bore tubing, along the axis of which is run a uniform platinum wire. Through suitably designed arrangements the electrical connections to this wire are brought out. A great care is taken to ensure minimisation and constancy of contact and stray resistances and in our arrangement their magnitude never exceeded 0.02 ohms. The outer wall is maintained at a constant temperature by circulating thermostatically controlled water in the surrounding jacket. The relevant constants of the column are given in Table I. The wire is maintained at different temperatures by passing appropriate currents through an arrangement which is energised by a number of high capacity lead accumulators. The column can be evacuated to high vacuum (10^{-6} cm of mercury) by means of a metal pumping plant comprising of a two stage rotary and a high capacity oil diffusion pump etc. The potential across the wire and current through it are measured by a sensitive Tinsley vernier potentiometer type $4363D$ and other accessories. The constants A and B of the platinum wire occurring in the relation

$$R_t = R_0(1+At+Bt^2), \qquad \ldots \quad (8)$$

are determined by a separate set of experiments. These are also required in the calculation of λ and are reproduced in table I. The detailed description is given by Saksena (1965).

TABLE 1

Geometrical and electrical constants of the conductivity column

Length of the platinum wire	91.56 cm
Radius of the wire (a) . ..	0 02463 cm.
Internal diameter of the column tube (2b) .	0.8544 cm.
External diameter of the column tube (2b′) ..	1.023 cm.
Resistance per unit length of the platinum wire at 0°C (R_0)	0.0054477 ohm/cm.
The constant A of the platinum wire	38.25×10^{-4}/°C
The constant B of the platinum wire	-49×10^{-8}/°C^2

In nut-shell the procedure amounts to measuring the power required to heat the wire at any arbitrarily chosen temperature with and without the test gas. To achieve this in practice measurements are taken, in vacuum and then with gas, of the resistance of the axial wire when a known current is passed through it. In Table II, we report the computed power at our directly observed points as a functions of temperature for vacuum and for five different pressures. The temperature of the hot wire in each case is identified by its resistance and assuming this variation to be in accordance with relation (8).

To compute λ for each pressure separately, W and W_r are plotted on a large graph paper versus temperature and by point to point subtraction a third curve is generated on the same plot for W_c as a function of temperature. Here W, W_r and W_c are the powers fed to the wire, with the gas, without the gas and conducted radially through the gas respectively. Next Stirling's formula is employed and the quantity $\left(\frac{dW_c}{d\theta}\right)$ is computed for equally spaced values of θ.

TABLE II

Record of power (W, Watt) consumed in the wire to maintain it at different temperatures (t, °C) in vacuum and at different pressures (p, cm of mercury)

t	W_r in vacuum	t	W ($p=10.2$)	t	W ($p=17.5$)	t	W ($p=29.3$)	t	W ($p=47\ 4$)	t	W ($p=60.5$)
62.7	0 0785	42.5	0 5850	39.2	0 4625	40.0	0 6133	46.5	2 671	40 4	0 6747
78.9	0 1640	60.8	2.607	63.1	2 538	57.1	2 595	56.2	4 036	60.7	2.582
109.1	0 3535	73.8	4.099	68 5	3 769	70 7	4 055	74.9	6 156	70 9	4 056
139.4	0 5909	94 0	6.422	88 3	6 096	87.8	6.102	94.6	9 155	89 1	6 172
184.3	1.067	114 1	8 870	114 7	9 301	111 1	8 943	124 6	12 81	112 5	9 046
224 3	1.596	142 6	12 50	141.0	12.70	137 3	12 40	149.1	16 72	142 6	12.99
262.9	2.261	176 8	17 16	174.3	17 17	171 2	16 92	189 5	22 56	172 4	16 96
301 2	3 166	217.5	23 09	211 2	22 34	205 2	21 86	235 2	29 62	213.1	22 97
344.2	4.286	263 2	30 27	258 9	29 88	253 7	29 74	284 1	38 24	261.4	30 64
370.3	5.300	320 3	40 12			302 6	38 15	378 4	55.93	308 0	38.78
400.5	6 072	375 6	50.72			359 5	48 71			371 2	50 66
452.2	7 206	459 6	68.54			418.4	60.71			466 2	69 52
455.7	8 668										
488 7	10 51										

TABLE III

Values of $10^5\lambda$ in cal cm^{-1} sec cm^{-1} deg^{-1} for Neon at different pressures, p, in cm of Hg as a function of temperature in °C

Temp.	$p = 10.2$	$p = 17.5$	$p = 29.3$	$p^* = 47.4$	$p = 60.5$
50	12.3	12.1	12.7	13.6	12.6
100	13.3	14.0	13.9	14.9	13.7
150	15.0	14.4	14.7	15.9	14.7
200	15.7	15.4	15.8	17.2	16.1
250	16.9	16.9	17.4	17.7	17.9
300	18.1		18.1	18.4	18.2
350	18.8		19.3	19.3	18.7
400	20.1		20.1		19.3
450	20.5				19.6

* This set is somewhat uncertain due to the instability of the electrical circuit.

The calculation of λ is now straightforward on the basis of relation (7). These values of λ are recorded in Table III and are shown plotted in Fig (1). It is relevant to point out here that while taking measurements at 47.4 cm of mercury the electrical circuit was somewhat unstable. This, we feel, might have caused uncertainty in the readings of unknown magnitude. We therefore in interpretation of our results do not give any weight to this set of data. Nevertheless, we have shown them plotted even in Fig. (1). It is interesting to note that the obser-

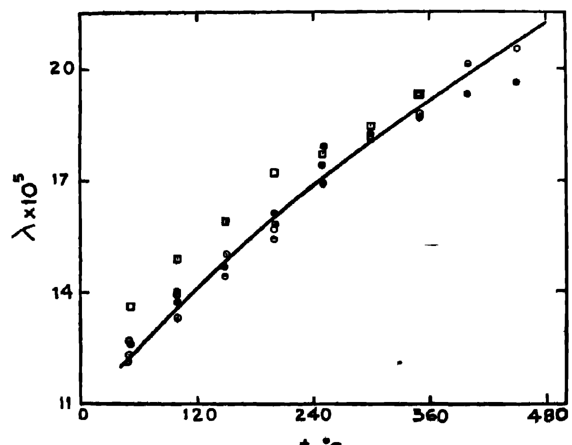

Fig. 1 : Plot of $\lambda \times 10^5$ (cal cm^{-1}sec^{-1}deg^{-1}) versus t(°C). Each set of points refer to a particular value of the pressure (in cm. of mercury). Thus, O, ⊖, ⊖, □ and ● refer to 10.2, 17.5, 29.3, 47.4 and 60.5 respectively. The continuous curve is obtained as a best compromise plot of all the other existing λ values,

vations even at a pressure higher than this value viz., 60.5 cm of mercury are in accord with the three sets of different observations all at smaller pressures. We hasten to state that all the four sets of λ values show no systematic difference of any particular type relative to each other as a function of temperature. The directly calculated λ values show a scatter of about 5 per cent and at various temperatures it is even smaller. Let us now discuss the important corrections to be applied to these computed λ values.

The corrections likely to be of importance for measurements by this method are : (a) convection, (b) temperature jump, (c) wall and (d) end effects. To discover whether the first two effects are involved in a particular measurement of this type there is an entirely experimental procedure possible This has been well known to experimentalists of this field and consists in taking measurements as a function of pressure. It was for this reason that we took measurements in the range 10.2 to 60.5 cm of mercury and for five different values of pressure. While taking the measurements it was also kept in mind to detect if there is any systematic variation, howsoever small, with the change in pressure. In the previous measurements pressure dependence was observed only around 2 cm of mercury, Saksena (1965). We thus conclude that for our apparatus and these operating conditions both convection and temperature jump effects are negligible. The calculation of wall effect is fairly well known and is described in detail by Saksena (1965). This effect which arises because of the finite conductivity of the material of the cold wall was found to be fairly small for our measurements. To quote for a numerical estimate it is only 0.3 percent at 50°C and rises slowly with temperature assuming a maximum value of 0.5 percent at 450°C

The last cor rection i.e. the end effect is probably the most important of all and unfortunate ly is least understood. This obviously appears because of the conduction of heat through the two ends of the hot wire and causes a nonuniform temperature distribution along the wire. As it is not simple to rigorously account for this shortcoming a brief discussion regarding its probable consequences will be in order. It may be stated that for a sufficiently long and thin wire this complication is likely to be small and we took the full advantage of this fact and kept the uncertainty on this score to the minimum The calculations of Saksena (1965) based on the theory of Gregory and Archer (1926) yielded that at 100°C for air the correction is about 0.6 percent and further as the conductivity increases the magnitude of this correction decreases. Thus, for neon it will be still smaller. However, it is not possible to apply this theory as the temperature further increases. Saksena (1965) has further tried to eliminate this effect by taking differential measurements on two columns identical in all respects except length and connected in series. It is believed that under such conditions the measurements taken refer to a small central region of the longer wire at a uniform temperature. His work with helium revealed that till 100°C the effect of end conduction on the finally calculated λ values is negligible We propose to consider both these points in our work at still higher temperatures than covered in the present effort. The situation which prompted us to adopt this approach consisted in a comparison of our measured λ values with those existing in the literature from conventional and accepted techniques. Gandhi (1966) has recently pooled together all the available data on rare gases as a function of temperature and recommended a set of best compromised smooth values In the figure we show these values by a continuous curve. It may be important to mention that there are considerable scatters in the data at different temperatures and a serious guidance is drawn from the measurements taken in this laboratory by a hot-wire cell, Gandhi (1966). It is particularly gratifying to note that the smooth curve posses well through our observed points lending thereby a very good support and reliance in our present measured values. We hope to further extend this work and bring to light the intricacies, if any, by suitably planned programme of work Thus, this work as well as earlier, Saksena and Saxena (1966), tend to establish this technique and its successful performance only upto the maximum temperature of 713°K. On the basis of this promise we are extending the scope of these measurements to still higher temperatures and will therein take into account all those corrections which may then become appreciable and are negligible in this temperature range. Our present experience based on the work in progress and going upto 1300°K indicate that this technique is capable of yielding sufficiently accurate and reliable values.

ACKNOWLEDGMENT

We are thankful to the Department of Atomic Energy, Bombay, and Council of Scientific and Industrial Research, New Delhi, for financial support. One of us (V.K.S.) also acknowledges the award of a research fellowship

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