THERMAL CONDUCTIVITY OF AIR AT LOW PRESSURES.

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IN the course of an investigation, still in progress, which involves the use of bolometers enclosed in a vacuum, irregularities in the equilibrium temperature of the bolometers were noted which were too large to permit a continuance of the work. It was obvious that the temperature variations were caused by variations in the pressure of the gas residues contained in the vacuum but as these pressure changes were found not to be wholly due to leaks and seemed to be unavoidable under the conditions of the original investigation, it was decided to make a separate study of the effect of pressure on the equilibrium temperature of a bolometer in order to ascertain whether or not there were any pressure at which the rate of change of the temperature with the pressure is a minimum.

The results of this subsidiary research seem to the writer to be of sufficient importance to warrant the publication of them separately especially as the main investigation of which this is a "by-product" will not soon be completed.

A body heated in a vacuum loses energy by conduction in its own material; by conduction due to the gas residues; by gas convection and by radiation. For small differences of temperature between the body and the enclosure the radiation may be taken to be proportional to this temperature difference and to depend in addition on the geometry of the system and on the nature of the radiating surfaces. For pressures of less than one tenth of a millimeter of mercury the energy loss by gas convection may be neglected in practice. The loss by conduction through the material of the body itself may be calculated from a knowledge of the thermal conductivity of the material and its geometry and by a proper choice of dimensions may be rendered small compared to the losses by other means.

The remaining mode of energy loss (gas conduction) is the only one which can depend primarily on the gas pressure.

It is known from the theoretical work of Maxwell and from the experiments of Kundt and Warburg that the thermal conductivity of a gas should be independent of the pressure so long as this is not too small and it is known that at very low pressures the conductivity is a function of the pressure.

M. v. Smoluchowski[1] has accounted for the latter fact on the principles of the kinetic gas theory by the aid of the assumption that while the "internal" conductivity is independent of the pressure there exists at the boundary wall a temperature discontinuity caused by imperfect thermal interchange and that this, itself a function of the pressure, plays an ever-increasing rôle in determining the energy flow as the pressure is reduced. When the pressure is so low that the mean free path of the gas particle is more than the distance which separates the body from its enclosure the "internal" conductivity no longer determines the energy flow even in part but the "external" conductivity is all-important and this M. v. Smoluchowski shows to be theoretically proportional to the gas pressure.

The results for the conductivity of air at low pressures obtained by calculation from the equilibrium temperatures of bolometers were in such good accord with the above theoretical considerations that it was decided to test them more accurately than had been possible in the preliminary experiment.

With this purpose the bolometer was abandoned for a platinum wire 30 cm. long and 0.005 cm. in diameter wound into a spiral and coated with platinum-black. This was mounted in the center of a glass bulb about 5 cm. in diameter connected to a Gaede molecular pump provided with a McLeod gauge capable of measuring gas pressures down to 1.5×10^{-5} mm. A tube containing cocoanut charcoal for use with liquid air to produce a vacuum free from mercury vapor was also connected with the tube containing the platinum spiral.

The spiral wire was sufficiently long in comparison to its diameter to make the energy loss by end-conduction negligible with respect to the losses by radiation and by gas conduction. The spiral formed one branch of a Wheatstone bridge, two of the remaining three branches of which were manganin coils of 1,000 ohms each. Opposite to the spiral was a manganin coil whose resistance was very slightly greater than that of the spiral and this coil was shunted with a variable high resistance so that the combined resistance of the branch could be made exactly equal to the resistance of the spiral.

After having determined the temperature coefficient of resistance of the platinum spiral in the usual manner it was found that the temperature of the spiral was very accurately proportional to the square of the current flowing in it provided the temperature rise of the spiral was not more than 20 to 30 degrees centigrade and provided the pressure of the gas in the bulb containing the spiral is maintained constant. This is to be

[1] Annalen der Physik, 35, p. 983, 1911.

expected since the rate of energy input is proportional to the square of the current and the energy outflow is proportional to the temperature difference between the body and the wall for small differences of temperature. The slope of the straight line connecting temperature rise and the square of the heating current depends only on the gas pressure in the enclosure, being in fact great for low pressures and small for high pressures.

It would seem thus that the slope of the temperature-(current)^2 curve might be brought into quantitative relation with the pressure corresponding to this slope and thus a law relating the gas conductivity with the pressure might be obtained.

This expectation has been fulfilled as a result of the observations reported further on.

The following table gives the results of a series of observations obtained with a blackened platinum wire in a glass enclosure which was maintained at a temperature of zero degrees centigrade by being kept in a Dewar flask containing cracked ice. In column 1 are tabulated the values of the gas pressure[1] in thousandths of a mm. of mercury. In column 2 are given the slopes of the temperature-(current)^2 function. Column 3 contains the reciprocal of the square of the values in column 2. Column 4 contains the values of column 3 diminished by the reciprocal of the square of the slope at zero pressure (this value was obtained by exterpolation). The last column contains the ratio of the values in column 4 to the corresponding values in column 1. The values in columns 2 to 4 inclusive are in arbitrary units.

Although there is a wide variation in the values in columns 1 and 4 column 5 shows a very fair degree of constancy.

In order to draw conclusions from this experimental result it is necessary to interpret the physical significance of the quantities $(1/s)^2$ and $(1/s_0)^2$.

If t represent the difference in temperature between the spiral and its enclosure when the current J flows we have the change in resistance of the spiral given by $r_t = r_0(I + \alpha t)$ where α is the temperature coefficient of the resistance of the material of which the spiral is made.

For small values of t it was found experimentally that $r \sim J^2$ or $r = sJ^2$ or $s = r/J^2$ where s is the slope given in column 2 of the table; hence $t = J^2 s/r_0\alpha$. If λ be the loss in calories per second per unit length per degree difference in temperature due to gas conduction and σ be the

[1] The pressures are not those at which observations were taken but are values taken from a smooth curve laid through the observation points. These latter were all so close to the smooth curve that the values in column 1 practically represent observation points and are more convenient for calculation.

loss due to radiation expressed in the same units and if the losses due to convection and to conduction in the material of the wire be negligible

TABLE I.

I. P. in Mm. Hg.	II. Slope.	III. $\left(\frac{1}{\text{Slope}}\right)^2$.	IV. $\left(\frac{1}{S}\right)^2-\left(\frac{1}{S_0}\right)^2$.	V. $\left(\frac{1}{S^2}\right)-\left(\frac{1}{S_0}\right)^2\div p$.
10×10^{-3}	1,670	$36\ \times10^{-8}$	$20\ \times10^{-8}$	$20\ \times10^{-5}$
20	1,355	54.8	38.8	19.9
30	1,155	75.5	59.5	19.8
40	1,000	100	84.0	21.0
50	893	123	107	21.4
60	820	146	130	21.6
70	770	169	153	21.8
80	735	185	169	21.1
90	695	207	191	21.2
100	663	228	212	21.2
110	629	252	236	21.4
120	610	269	253	21.1
130	591	286	270	20.8
140	571	306	290	20.7
150	552	327	311	20.7
160	538	346	330	23.0
170	523	365	349	23.5
180	511	383	367	22.0
190	500	400	384	21.0
200	485	424	408	22.0

the total loss from the wire when it is t degrees centigrade above its surroundings $((\lambda + \sigma)t)$ must be equal to the energy supplied by the current $(0.239J^2r_0/e)$.

Thus $t = 0.239J^2r_0/(\sigma + \lambda)l$ but since $t = J^2s/r_0\alpha$

$$(\sigma + \lambda) = \frac{0.239r_0^2\alpha}{ls} = k\frac{1}{s};$$

$$\therefore \quad \frac{1}{s^2} = \frac{1}{k^2}(\sigma + \lambda)^2.$$

Thus at pressure p

$$\left(\frac{1}{s_p}\right)^2 = \frac{1}{k^2}(\sigma + \lambda_p)^2 \tag{1}$$

and at pressure 0

$$\left(\frac{1}{s_0}\right)^2 = \frac{1}{k^2}(\sigma + \lambda_0)^2 \tag{2}$$

and the constancy of the values in column 5 of the table indicates that

$$(\sigma + \lambda_p)^2 - (\sigma + \lambda_0)^2 = k'p. \tag{A}$$

If we assume that at pressure zero the gas conductivity is also zero we have $\sigma^2 + 2\sigma\lambda_p + \lambda_p^2 - \sigma^2 = k'p$ or $2\sigma\lambda_p + \lambda_p^2 = k'p$. For very low pressures λ_p is small compared to σ for σ is independent of the pressure and hence in this case λ_p is proportional to the pressure. This is a result at which v. Schmoulouski arrived in his paper cited above.

If on the other hand the pressure is great the quadratic form of the function λ_p allows a practical independence of the pressure as Maxwell showed should be the case at high pressures. Thus equation A which satisfactorily represents the observations made with a blackened platinum wire in an enclosure of glass at constant temperature is in agreement with theoretical conclusions both at very low and at very high pressures.

In the former of the two cases the conductivity is proportional to the number of molecules present in unit volume. This is what we might expect if each molecule moved from the wire to the wall without colliding with its neighbors since this could only happen if the mean free path of the molecule were large in comparison to the distance between the wire and the wall, *i. e.*, at low pressures.

In the latter of the two cases the conductivity may be independent of the pressure because while the number of molecules in unit volume increases with the pressure the mean free path decreases in like amount so that the energy transfer may be independent of the pressure if the distance between the wire and wall be a great many times the mean free path.

It will be seen that the radiation σ may be calculated from equation (2). It may also be calculated as follows if we assume the wire to be a black body, cylindrical in form, of radius R and length 1 cm. The radiation loss per second of such a body is $2\pi lRA(T^4 - T_0^4)$ where A is the constant of the Stefan-Boltzmann law and T and T_0 are the absolute temperatures of the wire and the enclosure respectively. If the difference of these temperatures is small the loss may be expressed by $8\pi RT_0^3ltA$ and the loss per unit length per degree difference in temperature between wire and wall is

$$\sigma = 8\pi RAT_0^3. \tag{3}$$

(Since A is expressed in calories per sq. cm. per sec. σ will be expressed in calories per sec. per cm. length.)

The value calculated from this formula is 16.2×10^{-7} while that calculated from the data contained in the table is 20.3×10^{-7}. This difference is in part due to the fact that the area of the blackened wire is greater than that of the bare wire whose dimensions were used in the calculations by means of equation 3. As a further test as to whether I/s_0

is proportional to σ a series of observations was taken with the enclosure at 26 degrees centigrade. It was found that the value of the quantity k in equation A was unchanged although the value of $(I/s_0)^2$ was increased from 16×10^{-8} to 28×10^{-8}. The square root of the ratio of these two numbers is the ratio of the corresponding values of the radiation constants σ. Thus $\sigma_{26}/\sigma_0 = 1.32$. By equation 3 this ratio should be equal to the ratio of the cubes of the absolute temperatures, which is 1.31.

On the whole the calculations based on the assumption that the wire and the enclosure are black bodies are in very fair accord with the facts, but equation (A) is by no means restricted to the case of black bodies. In fact the equation shows that in the experimental determination of the gas conductivity it is advisable to employ a poor radiator so that σ may be small compared to λ.

With the object of testing further the validity of equation (A) experiments were undertaken with an unblackened spiral of platinum wire. The experimental procedure was altered as follows: Instead of observing the change of the resistance of the spiral for two different heating currents J_1 and J_2 at every pressure p the current J_p which must needs flow in order to raise the temperature an assigned amount was observed for every gas pressure.

Since $t = J^2 s_p / r_0 \alpha$ if t be kept constant $s_p \propto 1/J_p^2$ and by equations (1) and (2) $J_p^4 \propto (\sigma + \lambda_p)^2$ and $J_0^4 \propto (\sigma + \lambda_0)^2$. Thus for equation (A) to be true $J_p^4 - J_0^4$ must be proportional to the pressure p.

In practice the Wheatstone bridge which contained the spiral as one of its branches was always kept in balance so that the spiral was about 10 degrees C. hotter than its surroundings. To accomplish this the

Table II.

Pressure in Mm.	J_p^4	$(J_p^4 - J_0^4)$	$(J_p^4 - J_0^4) \div p$
16×10^{-3}	12.8×10^{-9}	12.3×10^{-9}	7.7×10^{-7}
9.2×10^{-3}	7.27×10^{-9}	6.77×10^{-9}	7.4×10^{-7}
7.6×10^{-3}	6.45×10^{-9}	5.95×10^{-9}	7.8×10^{-7}
7.4×10^{-3}	5.96×10^{-9}	5.46×10^{-9}	7.4×10^{-7}
5.2×10^{-3}	4.02×10^{-9}	3.52×10^{-9}	6.8×10^{-7}
4.86×10^{-3}	3.98×10^{-9}	3.48×10^{-9}	7.2×10^{-7}
3.2×10^{-3}	2.48×10^{-9}	1.98×10^{-9}	6.2×10^{-7}
2.5×10^{-3}	2.40×10^{-9}	1.90×10^{-9}	7.6×10^{-7}

resistances of the other three branches of the bridge were maintained constant and the current was adjusted to the proper value for each gas pressure at which observations were taken. This current was measured on a Weston mil-ammeter. This method of observation is, of course, not so accurate as that first employed as it involves the reading of a deflection instrument but it has the advantage of permitting rapid measurement. For some time past the writer has employed a heated platinum spiral in the manner just described as a substitute for the McLeod gauge in the pressure range below one one-thousandth of a millimeter of mercury and has found it possible to take about twenty pressure measurements with the spiral in the time required to take a single observation with the McLeod gauge. The following table includes the results of a characteristic series of observations taken by the last-described method:

As will be seen by comparison with Table I. the constancy in the last column is here not quite so satisfactory as in the case of the results obtained by use of the first method. This is undoubtedly due in part, as already mentioned, to the use of the mil-ammeter, and in part also to the fact that the gas pressures employed were much lower than in the first series and hence were less accurately determined by means of the McLeod gauge. It is evident however from a study of both the tables that within the limit of probable error the equation (A) is satisfied and that at low pressures the gas conductivity is proportional to the number of gas molecules present in unit volume.

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