A NEW METHOD OF DETERMINING THE TEMPERATURE VARIATION OF THE THERMAL CONDUCTIVITY OF GASES. I.

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SYNOPSIS.

Thermal conductivity of gases.—A new method of measuring the temperature variation of the thermal conductivity of a gas, by determining the temperature distribution in the gas contained between parallel plates maintained at different fixed temperatures, is described, and also a series of experiments made with air to test the method for temperature differences up to 500°. It was found that when the difference of temperature is not more than 100°, fairly accurate measurements may be made; but the larger the temperature difference, the more difficult it becomes to determine the temperature of the gas because of the large error due to radiation from the plates. If a thermo-element is used, as was done by the author, the error cannot be accurately computed because of the irregularities in the shape of the junction, hence the readings give only upper limits of the temperature coefficient. It is suggested that the temperatures might be measured with a fine wire resistance thermometer, but this was not tried. The disturbing effects due to convection may be made negligible.

Thermal conductivity of air.—The temperature coefficient between 20° and 500° was determined for air at atmospheric pressure, using the author's method. The temperature distribution was measured between an upper plate heated electrically and a lower water-cooled plate, by means of a small movable thermo-element. Because the large radiation corrections could not be determined accurately, the results for the higher temperatures can be considered only upper limits, but indicate that between 250° and 500°, the variation of the conductivity with the temperature is approximately linear. With an upper temperature of 100°, however, the results are more reliable and give a value for the coefficient (.00261) which is in good agreement with the results of other observers.

INTRODUCTION.

FROM a knowledge of the temperature gradient existing in a gas contained between two parallel planes maintained at different fixed temperatures, information may be derived concerning the thermal conductivity of the gas. As far as the writer is aware, no account of an investigation of such gradients has been published, except by Lasareff.[1] In Lasareff's experiments, gases at low pressures under gradients of only a few degrees per centimeter were investigated with the object of demonstrating the existence of a temperature discontinuity at the boundaries. In the present experiments the intention was to investigate steep temperature gradients in air at athospheric pressure, with the object of deter-

[1] Lasareff, P., Ann. der Phys., 37, p. 232, 1912.

mining the temperature variation of the thermal conductivity of air over a wide range of temperature. The present experimental evidence regarding the variation of thermal conductivity with temperature leaves much to be desired. Investigation has been largely confined to the region 0° to 100° C., and the results of various experimenters differ very widely.

If two infinite parallel planes are maintained at different fixed temperatures, the quantity of heat, Q, crossing unit area of any intermediate plane per second, is constant when a state of steady flow of heat is reached and is given by

$$Q = K\partial\theta/\partial z, \tag{1}$$

where K is the thermal conductivity of the gas and $\partial\theta/\partial z$ is the temperature gradient, z being the height above the lower plane.

The temperature gradient was obtained by noting temperatures at known points between the planes. The quantity Q was more difficult to measure with accuracy and hence absolute values of the conductivity were not sought for. However it seemed that relative values of K might be found from a knowledge of $\partial\theta/\partial z$ alone.

If we assume the variation of the thermal conductivity of air with the temperature, θ, to be given by

$$K = K_0(1 + \alpha\theta), \tag{2}$$

where K_0 is the thermal conductivity of air at the zero temperature and α may be called the temperature coefficient of thermal conductivity, then from (1) we obtain by integration

$$K_0(\theta + \tfrac{1}{2}\alpha\theta^2) = Qz. \tag{3}$$

On the other hand, if we assume the variation of thermal conductivity with the absolute temperature T to be given by

$$K = K_0T^n/T_0^n, \tag{4}$$

where n is a numerical constant, we have from (1)

$$z \propto T^{n+1}. \tag{5}$$

APPARATUS.

The apparatus used is shown in Fig. 1. It consisted of an upper hot plate and a lower cold plate between which air was enclosed by means of a glass ring. Temperatures in the air were measured by means of a thermocouple whose height was determined by means of a cathetometer.

The top plate was heated by an electric hot plate which was built up of sheets of asbestos slate as shown in Fig. 1. Coils of nichrome wire of No. 16 B. and S. gauge formed the principal heating element, the resistance of which, at room temperature was about 5 ohms. An auxiliary coil of nichrome ribbon was wound around the outside of the block of asbestos strips in order to compensate for the cooling at the edges.

Below the hot plate was placed a sheet of copper two millimeters thick

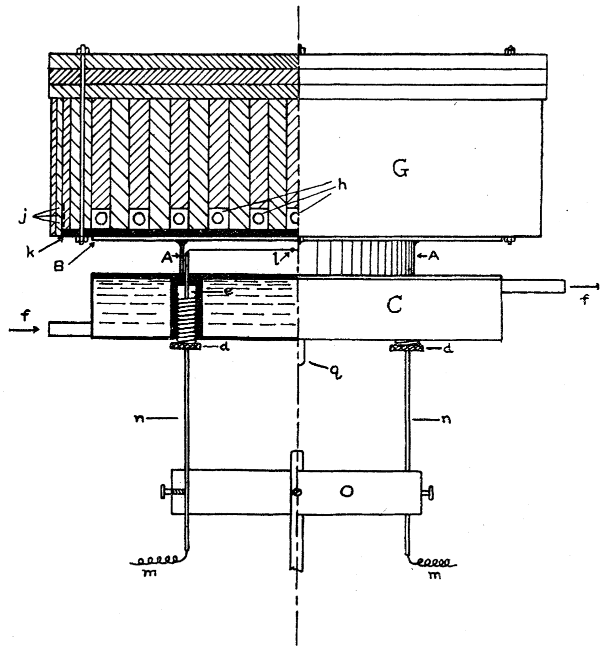

Fig. 1.

A, glass ring; *B*, glass plate; *C*, copper water-vessel; *ff*, water inlet and outlet; *e*, packing box; *d*, packing nut; *nn*, fine glass tubes; *l*, thermocouple; *o*, cross-arm; *mm*, thermocouple leads; *q*, side tubes carrying constantan wires; *g*, heater; *hh*, nichrome wire coils; *j*, auxiliary heating strip; *k*, copper equalizing plate. (Asbestos guard-ring strip removed to show details of apparatus.)

in order to equalize the temperature as much as possible. This sheet was in contact with a plate of glass, 14 cm. square and .17 cm. thick, which served as the top of the air chamber. To the glass plate was cemented a glass ring, 7.8 cm. internal diameter, 1.4 cm. high and .06 cm. thick. The cement used was "Vulcan Paste"[1] mixed with a little sodium silicate solution. This formed an airtight joint which withstood high temperatures. The lower edge of the glass ring was ground to give an airtight connection with a thick plate of copper, the surface of which was ground flat. This copper plate formed the top of a vessel through which water circulated.

[1] As supplied by the Pyrolectric Instrument Company of Trenton, N. J.

Temperatures were measured by means of a thermocouple made of 1 mil (.0025 cm.) constantan and 1.6 mil (.004 cm.) copper wires. The thermocouple was calibrated in steam, napthalene and sulphur vapors. The wires of the thermo-element were carried through small glass tubes which were moved up and down by means of a cross arm actuated by a micrometer screw. The temperature of the lower plate was given by two thermo-elements. The constantan wires of the latter were brought in through two tubes opening into the gas chamber just within the glass ring, where they were soldered to the copper plate. These tubes also served for introducing dry air or smoke into the chamber. An asbestos strip (not shown in diagram) closed the space between the upper and lower plates outside the glass ring, so that a guard ring was formed for the inner air vessel.

Any one of the thermo-elements could be connected with the rest of the circuit by means of suitable keys. The constant temperature junction common to all immersed in water and ice (or water only), in a Dewar flask. For the measurement of thermoelectric electromotive force a Kelvin-Varley slide, of total resistance 100,000 ohms, was used as a potentiometer with an Ayrton-Mather galvanometer. The error in temperature as indicated by the thermo-element was less than 0.3 per cent.

The distance of the centre of the thermo-element from the lower plate was determined by means of a cathetometer, the thermo-element being observed through the glass ring and small holes covered with mica in the asbestos outer casing. The error in determination of the height of the thermo-element was less than .02 mm. To allow for possible errors due to striae in the glass ring, a calibration was made. When the apparatus was cold the thermo-element was kept taut by small weights and its height adjusted by the micrometer screw which moved the cross arm. Readings taken on both micrometer screw and cathetometer agreed within the limits of observation. As the glass ring was in a uniform temperature gradient when the upper plate was heated, it was assumed that it introduced no error.

The current heating the upper plate was allowed to run for two or three hours to allow the temperature to attain a steady state before readings were begun. Although the voltage of the D.-C. circuit was not very steady, the temperature at a fixed point near the upper plate when at about 400° C., did not change by more than one or two degrees in two hours. This small progressive change could easily be allowed for in plotting curves.

A rough measurement of Q, the heat carried across the gas per square centimeter per second, was also made. Thermocouples placed in the intake and outlet of the lower plate, gave the difference in temperature between the inflowing and outflowing water, while the water flowing through the apparatus in a given time was noted. The total flow of heat, so found, was divided by the total area of the glass plate. The above values of Q were only used in determining a radiation correction and were not required with any great accuracy.

Convection.

The arrangement of the gas in layers of density diminishing with height tended to ensure stability. The guard ring was also of assistance in this regard. The temperature along horizontal planes was fairly uniform. The region within the ring was explored by a thermo-element moved along a horizontal plane over nearly two thirds of the breadth of the vessel. Variations of temperature were found to be less than 4° C., which could easily be accounted for by the errors in cathetometer settings. Tobacco smoke was blown into the vessel through one of the side tubes. The eddy motion quickly died out, and the smoke cloud was observed to settle gradually down to the bottom of the vessel in a well defined horizontal layer. No sign of movements due to convection could be noted. The agreement and reproducibility of the observations also indicate that convection was negligible in these experiments.

Radiation.

The errors due to radiation, however, are not negligible. The thermo-element, at a temperature intermediate between those of the upper and lower plates, may be receiving more heat than it loses by radiation, and consequently its temperature will rise above that of the surrounding gas until the losses by conduction and convection, (*i.e.*, by "free convection"), equalize the gain by radiation. At other positions the thermo-element may be losing more heat by radiation than it receives, with the result that its temperature will fall below that of the surrounding gas.

A method was developed for determining the correction to be applied to the temperature indicated by the thermo-element, in order to find the temperature of the surrounding gas. As the detailing of this method would introduce too much matter foreign to the main object of this paper, its explanation is embodied in a separate paper, in which the application of the method to the present case is given in full.

Observations.

A series of observations of the temperature and height of the thermo-element was made at each of four different heating currents, *i.e.*, at four different temperatures of the upper plate. As it soon became evident that radiation had an important effect on the temperature indicated by the thermo-element, the glass plate was silvered and four series of observations made using the same power inputs as before. The glass plate was then covered with soot and similar series of observations taken.

At a given heating current the number of observations made during a single run was between 20 and 40, the thermo-element being twice moved over the whole distance between the plates. The observations were plotted on a large scale with heights of the thermo-element above the lower plate as ordinates, and temperatures (referred to lower plate as zero) as abscissæ. When a smooth curve was drawn through these points they were found to lie on, or very close to, the curve.

Two series of observations were taken with the same current inputs, one with ordinary room air, and the other with air dried by passing through $CaCl_2$ and P_2O_5. One curve was found to fit both series of

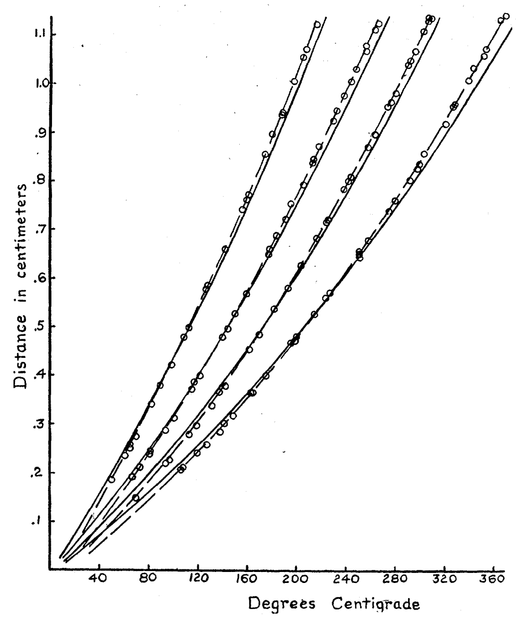

Fig. 2.

observations equally well. Furthermore no deviations from the curve could be found if the tubes leading to the gas chamber were open to the atmosphere, and in the latter experiments these tubes were left open.

As the actual observations are voluminous, they are not given in detail. As an example of the results obtained a specimen series of curves is shown in Fig. 2. In these experiments the glass was silvered. The broken lines are smooth curves drawn through the points representing actual observations, while the unbroken lines are the same curves corrected for radiation by the method referred to.

It will be seen that the uncorrected curves do not pass through the origin, showing that a thermo-element indicates a temperature discontinuity at the boundary between plate and gas. The corrected curves however pass much closer to the origin. This is strong evidence that the corrections are of the right order of magnitude, for at atmospheric pressure no appreciable discontinuity is to be expected.

The results were tested on the assumption (2). If assumption (2) is correct, the temperature-distance curves (eq. 3) would be parabolic. In order to test this, temperatures were plotted as abscissæ, and distances from the lower plate divided by the corresponding temperatures as ordinates. The points were found to lie approximately on straight lines, showing that the curves were approximately parabolic. The values of α were at once obtained from these lines, since $\alpha = -2/c$, were c is the intercept on the axis of abscissæ. Fig. 3 is given as an example of the

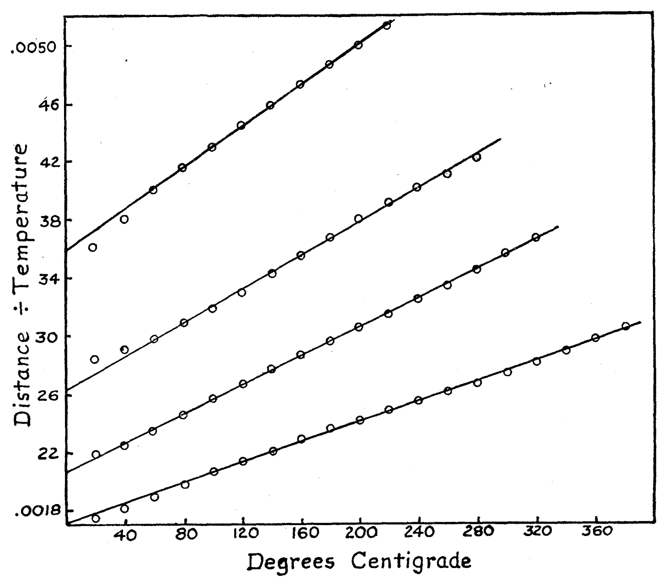

Fig. 3.

results obtained. The data used in Fig. 3 were taken from the corrected curves of Fig. 2.

The corrected curves of Fig. 2 were also tested on the assumption (4).

On plotting T^{n+1} against z approximate straight lines were also obtained when a suitable value of n, chosen by trial and error, was used.

Thus the variation of the thermal conductivity of air with temperature seemed to be expressed by either assumption (2) or (4), within the limits of error imposed by the present experiments.

RESULTS AT HIGH TEMPERATURES.

The results obtained in these experiments are given in the following tables.

TABLE I.

Clear Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00451	.00495	1.30	226	....	.50
6.35	.00457	.00564	1.20	318	....	.48
7.62	.00428	.00556	1.15	393	....	.40
8.42	.00517	.00644	1.12	438	....	.38

TABLE II.

Silvered Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00394	.00394	1.32	277	.0418	.247
6.35	.00435	.00466	1.20	328	.0831	.374
7.62	.00488	.00550	1.17	393	.143	.464
8.42	.00445	.00466	1.05	456	.191	.432

TABLE III.

Blackened Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00490	.00484	1.32	246	.0593	.544
6.35	.00544	.00602	1.30	319	.102	.523
7.62	.00500	.00572	1.12	413	.143	.407
8.42	.00500	.00600	1.12	483	.187	.363

The first column shows the current in amperes passing through the heating coil. In the second column are given the values of α determined from the corrected observations. For purposes of comparison, the column headed α' gives the values of the temperature coefficient obtained from the uncorrected observations. Values of n from the corrected observations are given in the fourth column. In order to show the range of temperature involved, the temperature of the upper plate, obtained by extrapolation of the curve, is shown in the fifth column. In the next column is shown Q, the quantity of heat carried across the gas, in calories per square centimeter. In the last column are given the values of ϵ, a quantity determined from Q, as explained in the paper on the radiation error.

Unfortunately, measurements of Q were not made during the experiments with clear glass and the values of ϵ in this case are only estimated.

The only other investigation of the variation of K with θ for temperatures higher than 100° C. is that of Stafford.[1]

These results would give mean values of α over the range covered in the above experiments from .0030 to .0042.

It will be seen that the values of α given in Tables I., II., and III. are considerably higher than those which may be calculated from Stafford's experimental data.

The values of n are more concordant among themselves and decrease with increasing temperature range.

The values of α and n are dependent upon the corrections for radiation applied to the original curves, the corrections in some cases materially altering the original values. The probable errors involved in the assumptions made in evaluating the corrections are large. The largest error is probably in the value of the "effective diameter" of the wires of the thermo-element. In the process of fusing the wires a comparatively large lump of metal was unavoidably formed at the junction. The assumption was made that the effective diameter of the wires was that of the larger wire, viz., 1.6 mils. This value is very unlikely to be too large but may be considerably too small. An increase in the effective diameter of the wire would require larger corrections for radiation, which would decrease further the values of α. For instance, if the radiation corrections for the last series of observations for blackened glass (Table III.) had been doubled, the value of α would have been reduced from .00500 to .00357.

In view, then, of the uncertainties involved in the determination of the radiation corrections, the values of α given can be considered only as upper limits. From their variation with the temperature range it seems evident that a simple formula of the type

$$K = K_0(1 + \alpha\theta)$$

is not sufficient to express the variation of thermal conductivity with temperature over the range employed (20° to 500° C).

A formula of the form,

$$K = K_0(1 + \alpha\theta + \beta\theta^2)$$

would probably be needed to express approximately the variation of K with θ over this range, but with the uncertainty of the given values of α it would be futile to evaluate the coefficient β.

[1] Stafford, Zeits. für Phys. Chem., 77, p. 67, 1911.

Summing up the results of measurements of temperature gradients over a wide range, it may then be stated that a two power formula seems necessary in order to express approximately the variation of thermal conductivity of air with temperature. Owing to the errors involved in evaluating a correction for radiation, only upper limits to the first coefficient can be obtained from the present measurements. These values are given in the column headed α in Tables I., II. and III. above.

A formula of the form

$$K = K_0 T^n / T_0^n$$

also seems to express approximately the variation of K with temperature. The values of n obtained are given above. They are, however, not independent of the temperature range, and can be regarded only as upper limits owing to the uncertainty in the radiation corrections.

Temperature Coefficient between 15° and 100° C.

If the temperature range be decreased, the radiation corrections become smaller, and errors in them have less effect on the temperature coefficient. Accordingly experiments were carried out over the range 15° to 100° C.

The electrically heated plate was replaced by one of copper over which steam was made to circulate, while a potentiometer of low resistance was substituted for the Kelvin-Varley slide. The temperature of the lower plate was about 15° C. Both silvered and blackened plates were used.

The results obtained are given in Table IV.

Table IV.

Silvered Glass.		Blackened Glass.	
α.	α'.	α.	α'.
.00256	.00292	.00243	.00256
.00281	.00289	.00265	.00297

The mean of the given values of α is .00261.

As the value of α is small, slight variations in the shape of the curves have considerable effect on this value. Hence very close agreement in the individual values of α could not be expected and the variations shown in Table IV. may be considered as reasonable for this method. The probable error in the above value of α is about 4 per cent.

The mean value of α' is .00283. The introduction of the radiation correction thus lowers the value of the temperature coefficient 8.4 per cent. Over the range 15° to 100° C. the error due to radiation is thus comparatively small and the temperature coefficient over this range should be measurable with much more accuracy than over the wider range. An error of nearly 50 per cent. in the radiation correction would only change the value of the temperature coefficient by about 4 per cent., which is approximately the accuracy afforded by the present measurements.

Some recent determinations of α by other observers over the range 0° to 100° C. are given below.

Eckerlein, *Ann. der Phys.*, 3, p. 120, 1900	.00362
Schwartze, *Ann. der Phys.*, 11, p. 303, 1903	.00253
Pauli, *Ann. der Phys.*, 23, p. 928, 1907	.00197
Eucken, *Phys. Zeits.*, 12, p. 1101, 1911	.00271
Mean of these values,	.00271

Of these results the most trustworthy is that of Eucken, which agrees fortuitously with the mean of the four.

Thus it will be seen that the result of the present determination is in good agreement with the mean of other observers. This would show that the method described in this paper will give satisfactory results if the radiation corrections are relatively small, *i.e.*, if the temperature range is not too large.

REMARKS.

The satisfactory results obtained by this method when radiation corrections were small would indicate that by measuring the temperature gradients over a narrow range of temperatures the temperature variation of thermal conductivity might be determined up to a high temperature, in a series of steps.

There is also the possibility of using a small stretched wire as a resistance thermometer, instead of a thermocouple, and determining the radiation correction as before. This would have the advantage that a uniform wire might be used, doing away with the unavoidable lump of metal at the thermo-junction and thus making the effective diameter of the wire quite definite. The heat gained by the wire by radiation would still have to be calculated, however.

Experimentally, this method would have grave disadvantages, involving as it would, "line" instead of "point" temperatures. It would be necessary to keep the wire parallel to the plates, while the required potential leads would introduce further difficulties.

One point is clearly brought out in the present work, viz., the unreliability of temperatures as indicated by a temperature-measuring device placed in a gas in the presence of surfaces at temperatures differing considerably from that of the body of the gas.

The problem of temperature measurement in such cases is of considerable practical importance. That the radiation error involved may be large does not seem to have been emphasized in the past. In a publication recently received, however, Kreisinger and Barkley[1] discuss this point in considerable detail from the practical standpoint of the measurement of the temperature of gases in boiler settings. By using thermocouples of different diameters and exterpolating to zero diameter. Kreisinger and Barkley showed that the radiation error of a large thermocouple under practical working conditions might be as much as 150° C., in a gas at a temperature of about 1000° C.

In conclusion the writer wishes to express his thanks to Dr. L. V. King for placing the facilities of the Macdonald Physics Building at his disposal and for directing this research. He also wishes to express his gratitude to the Honorary Advisory Council for Scientific and Industrial Research of Canada, under whose auspices the earlier part of this work was done.

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[1] Kreisinger and Barkley, Bull. U. S. Bureau of Mines, 145, 1918.