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V. On a Method of Determining the Thermal Conductivity of Metals, with Applications to Copper, Silver, Gold, and Platinum.

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Communicated by Lord KELVIN, P.R.S.

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OF the different methods hitherto employed for the determination of thermal conductivity of metals, only those which were elaborated by FORBES and by ÅNGSTRÖM have been successful in giving absolute results with fair approach to accuracy. The two methods, in the hands of these and subsequent experimenters, have given closely concordant results, both for copper and for iron. They, however, possess the disadvantages of being exceedingly elaborate, requiring, as they do, very extensive preparations and comparatively large masses of the metals which are to be tested. For this reason, only the less costly metals can be tested, as it would be impracticably expensive to obtain a bar of gold or platinum, for example, a metre or more in length, and perhaps 2 square centims. section.

The method used in the present investigation (for which a grant of £50 was obtained from the Government Research Fund) is free from these objections. It was suggested by Lord KELVIN as far back as thirty years ago, about the same time that the late Principal FORBES began his experimental inquiry as to whether thermal conductivity varied with temperature. The chief advantages of this method are that (1) it is much simpler than the others; (2) a test of the conductivity of any metal can be made in two or three hours; and (3) (perhaps most important of all) only a few grammes of the metal are necessary. Thus, even the rarest and most expensive metals can be tested, at very moderate cost.

The method is essentially the experimental realization of the theoretical conditions implied in the fundamental formula

$$\mathbf{Q} = k\mathbf{A} \frac{v - v_0}{l} t$$

where the symbols have their usual meaning. The metals to be tested are made in the form of wires of circular section. One end is kept at a constant temperature v, and the flow of heat Q, in a given time t, is measured. The length and section being known, all the data are obtained for the determination of the absolute value of 30.5.95

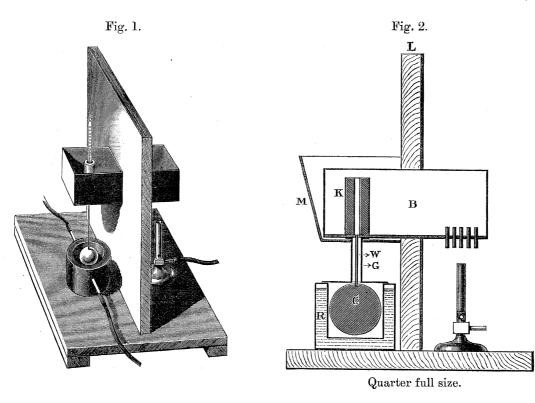


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MR. J. H. GRAY ON A METHOD OF DETERMINING

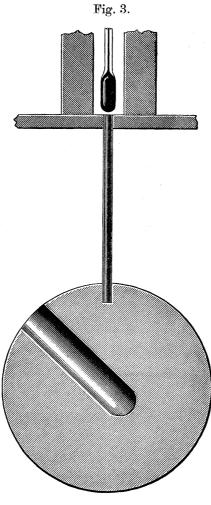
the thermal conductivity. It will be noted that this value is the proper mean conductivity corresponding to the range of temperature between the ends of the wire.

Fig. 1 is a perspective drawing of the apparatus which has been used in the tests of this method. Fig. 2 is a section (all the parts being drawn quarter full size) containing the axis of the wire to be tested. Fig. 3 is a section, drawn full size, through the middle of the apparatus, in a plane perpendicular to the section in fig. 2, and showing in greater detail the wire, calorimeter ball, and that part of the heating box at which the wire is soldered.



Referring to fig. 2, W is the wire to be tested. The upper end of W is soldered into the bottom of the copper box B, and the lower end into the solid copper ball C, the diameter of which is 5.5 centims. The sides of the copper box B are of thin sheet copper, and the bottom of copper, 3 millims. thick. B is supported at the middle by being fitted into a rectangular hole in a wooden screen, L, of dimensions 60×60 centims., by 2 centims. thick. In the hole of the copper block K, a small thermometer is inserted for measuring the temperature of the other end of the wire. The box B is filled with water and kept boiling briskly. The ball C is the calorimeter by which the amount of heat conducted by the wire W is measured. In order to measure the temperature of C, a very sensitive thermometer, which can be read to one-fortieth of a degree Centigrade, is inserted in a hole drilled in C. This hole reaches to a depth of 3.6 centims. from the circumference of the ball. The bulb of the thermometer in the ball is surrounded by water or mercury. Surrounding

the heating box, B, is an asbestos covering, M, to prevent heat from reaching the calorimeter from the sides of the box. In order to keep the temperature of the air surrounding the calorimeter constant, the latter is surrounded by a water-jacket, R, through which water at the temperature of the air is kept circulating. This waterjacket is simply a cylindrical vessel, made of copper, with double walls, between which the water circulates. The inside diameter is about 1 centim. greater than that of the ball. The top of the water-jacket is covered with three or four layers of

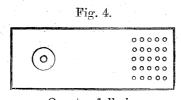


Full size.

paper, so that the air surrounding the ball is completely separated from the outside air, and is kept at a constant temperature. Surrounding the wire, all along its length, is a tube of cardboard, G, of inside diameter 1 centim. Between the wire and the inside of the tube cotton-wool is loosely packed, so as to prevent, as effectually as possible, circulation of air about the wire.

From fig. 2 it will be seen that the heat from the Bunsen is prevented from

reaching the wire or the ball by the wooden screen L. In the bottom of the box, just above the Bunsen, are riveted a number of copper pins, so as to catch and distribute the heat of the burner. Fig. 4 shows a plan of the box.



Quarter full size.

It will be convenient to classify the sources of error that may affect the results, and to deal with them at this point.

1. There is, unless proper precautions be taken, loss of heat due to radiation from the surface of the wire, and therefore the value obtained for the conductivity will be too low.

2. The temperature indicated by the thermometer in the hot water may not be the same as that of the end of the wire at the point where it enters the box. Also, the temperature of the ball may not be the same throughout.

3. The thermometer may not indicate the average temperature throughout the ball.

- 4. There may be a lag in the thermometer.
- 5. There may be some error due to the solder at the ends of the wire.

1. Loss of heat due to radiation from the surface of the wire. As this was the most obvious source of error, a long time was spent and much work done in investigating it.

The cardboard tube G (fig. 2) was found to be thoroughly efficient in preventing radiation. It can be very easily made by rolling a long strip of paper, which has been previously gummed on one side, several times round a circular rod of a centimetre diameter. The length of the tube is a little less than that of the wire. After the gum has dried, a slit sufficiently wide to admit the wire is cut parallel to the length. A circular piece of cardboard is fixed with gum to one end of the tube, as a flange for attaching the tube to the bottom of the heating box. After it has been arranged that the wire is in the central line, cotton-wool is put loosely in and the slit closed up with gummed paper. The small volume of air in this tube takes almost immediately the temperature of the wire all along its length.

To test the efficiency of the tube, a large number of experiments was made, the results of which are given further on (pp. 180, 181). It is clear that for a given difference of temperature between the ends, the loss by radiation from the surface of a wire of given diameter will be greater the greater the length. If, then, there be no error which becomes less the greater the length, and thus compensates for the radiation error, a sufficient test of the efficiency of the tube will be to determine the conductivity with different lengths of the same wire. The shorter lengths ought to give a distinctly higher value, since the radiation from the surface is not only less than in the longer lengths, but the quantity of heat conducted along the wire per second is greater, and therefore the percentage error due to radiation rapidly diminishes.

In order to determine a superior limit for the error due to loss of heat by radiation, a calculation is made below. The numbers used are taken so as to be as unfavourable as possible, and give a value much higher than what would practically turn out.

In the case of copper wire, the surface was always somewhat tarnished, so the emissivity may be taken as intermediate between those of polished and blackened copper, that is 0008. The diameter and length of wire were respectively $\cdot 2$ centim. and 4 centims. The temperature at the hot end was 98° C., at the cold end 14° C. The curve of temperature along the wire being logarithmic, the mean temperature will be considerably less than half the sum of the highest and lowest temperatures, which would assume that the curve is a straight line passing through the highest and lowest points. Take, however, the curve to be a straight line; then the mean temperature above that of the air is 42° C. The quantity of heat Q, lost from the surface S, of emissivity E, in one minute, is

 $Q = ES \times 42 \times 60$ = 1.91 C.G.S. units approximately.

The quantity of heat conducted along the wire during this minute, as taken from one of the tests, was 5×68.9 , 5 being the rise in temperature, and 68.9 the capacity of the calorimeter. The maximum percentage error due to radiation in a length of 4 centimes. is therefore 5.5 per cent. This is on the assumption that there is no jacket round the wire, but even then the actual loss would probably be less than 3 per cent. if currents of air be avoided. This rough calculation shows that radiation from the surface of the wire need not be considered as an objection to the method.

2. Possible error due to the fact that the thermometers are not actually at the ends of the wire, and so may not be indicating the proper temperatures.

The effect of this error would also be to give too low a value for the conductivity. To guard against this the bottom of the box is made very thick, and the large block K (fig. 2) is added so as to hold the thermometer. The difference of temperature between the inside and outside surfaces of the bottom of the box is certainly exceedingly small, if as much heat as the wire can take away is supplied to it. Since the heat is supplied by boiling water, it is, however, possible that the copper conducts so quickly that there is always a layer of water, it may be thin, immediately in contact with the metal at a very much lower temperature than 100° C. This point is particularly emphasized by Lord KELVIN in volume 3 of his Collected Papers, where he remarks upon the exceedingly low values obtained by CLÉMENT and by PÉCLET for the conductivity of copper. These experimenters both attempted to measure the conductivity by keeping one side of a slab of the metal in contact with water at a constant temperature and measuring the rise in temperature of a known

MDCCCXCV.---A.

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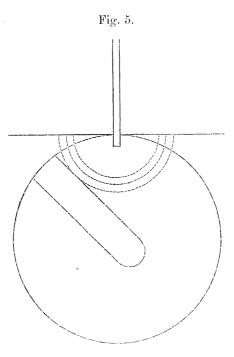
quantity of water in contact with the other side. The result was that CLÉMENT'S value was 200 times too small, while PÉCLET, who tried to avoid CLÉMENT'S error by having the water violently stirred, succeeded in obtaining a value six times too small. With the large surface to carry away the heat, PÉCLET'S method is useless for any substance having so high a conductivity as even the worst of the metals, since the stirring could never be rapid enough without introducing fresh complications.

The direct tests applied to determine this error in the present investigation showed that the temperatures on the inside and outside of the bottom of the box were the same.

The following approximate calculation serves to show the order of magnitude of the error due to the assumption that the thermometer in the ball indicates the temperature of the end of the wire.

It is clear that the difference of temperatures between the wire where it enters the ball, and the thermometer will be much less than that found as follows :---

Take the case of a wire carrying heat to an infinite block of metal whose surface is



plane, and remark that the isothermals in the block would be hemispherical surface (fig. 5) having for their common centre the point where the axis of the wire enters the ball, and suppose the flow of heat to be steady.

Let

K = conductivity of the wire,k = ,, ,, ball,a = radius of the wire,b = ,, ,, ball.

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Then the quantity of heat that flows through any hemispherical surface distant r from the end of the wire is

$$\mathbf{Q} = -k \frac{dv}{dr} \, 2\pi r^2 \,;$$

and, since the flow is steady

$$\frac{d}{dr}\left(-k\frac{dv}{dr}\,2\pi r^2\right)=0.$$

Hence

$$r^2 \frac{dv}{dr} = C_1,$$

which gives

$$v = \mathbf{C}_1 r^{-1} + \mathbf{C}_2.$$

For r = a let v = V, and for r = b let $v = \theta$.

Hence

$$v = ab \frac{\nabla - \theta}{b - a} r^{-1} + \frac{\theta b - \nabla a}{b - a}$$

whence

$$-\frac{dv}{dr} = ab \frac{\mathbf{V} - \theta}{b - a} r^{-2};$$

 $\mathbf{Q} = 2\pi k \, \frac{\mathbf{V} - \theta}{b - a} \, ab.$

and

Also

$$\mathbf{Q} = (\mathbf{V}_1 - \mathbf{V}) \, \frac{\pi a^2 \mathbf{K}}{l}$$

where V_1 is the temperature at the hot end of the wire, and l the length of the wire.

Since V is the temperature of the wire just where it enters the ball, and θ the temperature at the centre of the ball, $V - \theta$ is certainly much greater than the error, a superior limit to the magnitude of which we wish to ascertain. The heat which flows through the wire must be equal to that which flows into the ball; therefore

$$(\mathbf{V}_1 - \mathbf{V}) \frac{\pi a^2 \mathbf{K}}{l} = 2\pi k \frac{\mathbf{V} - \theta}{b - a} ab,$$

whence

$$\begin{aligned} \mathbf{V} - \theta &= (\mathbf{V}_1 - \mathbf{V}) \, \frac{a}{2l} \, \frac{\mathbf{K}}{k} \frac{(b-a)}{b} \\ &= - \left(\mathbf{V} - \theta + \theta - \mathbf{V}_1\right) \frac{a}{2l} \, \frac{\mathbf{K}}{k} \frac{(b-a)}{b}, \end{aligned}$$

and, therefore,

$$\mathbf{V} - \theta = (\mathbf{V}_1 - \theta) \frac{\frac{a}{2l} \frac{\mathbf{K}}{k} \frac{(b-a)}{b}}{1 + \frac{a}{2l} \frac{\mathbf{K}}{k} \frac{(b-a)}{b}}.$$

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In this case $V_1 = 100^{\circ}$ C, $\theta = 15^{\circ}$ C, and, since the copper of the wire and ball were the same, K/k = 1; b = 27 millims., a = 1 millim.

Take l = 8 centims.; then,

$$\mathbf{V} - \theta = 85 \frac{\frac{1}{160} \frac{26}{27}}{1 + \frac{1}{160} \frac{26}{27}} \doteq \cdot 5^{\circ} \mathrm{C}.$$

Take l = 3 centims., which is less than the shortest length used ;

$$V - \theta = 85 \frac{\frac{1}{60} \frac{26}{27}}{1 + \frac{1}{60} \frac{26}{27}} \doteq 1.3^{\circ} C$$

Therefore 1.3° C. is greater than the extreme possible error made with the copper wire, that is 1.3 in 85, or about 1.5 per cent.

Several attempts were made to obtain a direct test of this by applying a thermoelectric junction to the wire just at the point where it entered the ball. Owing, however, to the large mass of the ball which had to be heated, it was found most difficult to solder the thin wires of the thermo-electric junction at the required place, and, after several unsuccessful attempts, it was given up, as the indirect proof supplied by using different lengths of wire seemed quite satisfactory.

3. The thermometer in the ball may not indicate the average temperature.

This also would be tested by using different lengths of wire, and, as will be seen, the results show that there was no substantial variation.

4. Lag in the thermometer which measures the rise in temperature of the ball. Here again different lengths will be a test. Also, in case that the water round the bulb of the thermometer caused the lag, mercury was substituted, but no difference in the result was obtained.

5. The solder at the ends did not cause any difference of value for different lengths.

The method of conducting a test is as follows.

Take a length of not more than 8 centims. of the wire. As it is very easy to obtain any diameter, it will be convenient to have a hole bored in the bottom of the heating box, just below the thermometer, of diameter rather more than 2 millims., and depth 3 or 4 millims. The heating box must be brazed together, otherwise it is apt to fall to pieces when the wire is being soldered in. The latter process can be done with ordinary solder.

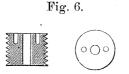
The mass of copper in the box being considerable, it is rather a troublesome matter to solder the wire into it, as the whole box has to be heated. For this reason a soldering iron cannot be used. The box is most easily heated by a blow-pipe flame and the wire then inserted. The extra solder is then cleared off, so as to give a definite point from which to measure the length. After this end is fixed, the other end is soldered in a similar manner to the copper ball, and in the latter case fusible solder melting at about 100° C. will do quite well.

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then

It was, however, found that the method of soldering just described, and used in this investigation, was very troublesome, and required some practice. If new apparatus were being made, it would certainly be much more convenient to make an alteration in this respect.

The following plan would make the soldering of the wire a very easy process, instead of, as described, a difficult one. Six copper plugs, each of the shape shown in sectional elevation and plan in fig. 6, might be made, 8 millims. in length,



and 1 centim. diameter, so as to screw into a corresponding hole in the bottom of the heating box; and six similar plugs might be made for the ball. In each of the plugs the central hole might be made of a different diameter, varying from 2 to 4 millims. In this way, wires of different diameters could very easily be soldered into the suitable plugs, which could then be screwed, first the one end into the ball, then the other end into the box. The two side holes shown in fig. 6 are for the purpose of facilitating the screwing in of the plugs. By screwing into the ball first, the possibility of twisting the wire is avoided. It is advisable not to use wire of diameter much less than 2 millims., for, in wires of less diameter, the length required to give a readable rise of temperature per minute becomes inconveniently small, unless the calorimeter ball is made very small.

The calorimeter ball most frequently used in the present work was turned from the solid, and is 5.5 centims. in diameter. This was found to be a very convenient size for the metals of high conductivity—for example, gold, silver, and copper. Any length from 4 to 8 centims. of wires of these metals may be used without making it difficult to read the rise in temperature per minute. It is not advisable to use lengths shorter than 4 centims., as there is then a danger of the waterjacket being too near the heating-box, but it is better to use a smaller ball, say of 4 centims. diameter, for metals of lower conductivity. For metals having conductivities between 1.0 and 0.7 C.G.S. units, the large ball was found to be quite convenient; for lower values the smaller ball was used. The object aimed at was to arrange the dimensions so as to enable an experiment to be finished in less than half an hour from the time that one end was made hot by the boiling water.

After the wire has been soldered in, the box is placed in the screen L (fig. 2), and fixed by any convenient means, so that the wire hangs vertical, and the asbestos cover is put over the box. The cardboard tube, having been made of suitable length, and slit along its length, is now slipped round the wire, and, after a little cotton is loosely packed in, the slit is closed up by means of a strip of gummed paper.

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The wire is now completely enclosed in this tube, and loosely surrounded by cotton wool.

The thermometer is placed in the hole in the ball, and a little water put in to fill up the hole. The water-jacket may then be raised so as to surround the ball, and the top of the water-jacket must be covered with two or three sheets of paper, holes having been cut in these, so as to admit the wire and thermometer.

It was found best to make these preparations a few hours before the actual test was begun, so as to allow the system to take up a permanent temperature. When it has been ascertained that this temperature has been reached, a reading is taken from the thermometer in the ball. The thermometer used was most carefully made and calibrated for the tests by Mr. OTTO MÜLLER, of Glasgow. The whole length of the stem is 15 centims., and it is marked off to read twentieths of a degree from 9° to 20° C. Each division is a half millimetre, so it is perfectly easy to read to onefortieth of one degree.

Before beginning the test, the water-jacket is lowered, and a vessel containing ice and water raised so as to cover a part of the ball. By this means the temperature of the ball is lowered by 6° or 7° below that of the air. While this is being done, the boiling water is poured into the box, so as to nearly fill it, and the Bunsen lamp lit. The water soon begins to boil rapidly, and the thermometer (which is 12 centims. long and reads from 95° to 105° C.) indicates a constant temperature, usually 97° or 98° C. When the temperature of the ball has been lowered 6° or 7° , the ice and water are taken away, and the ball is carefully dried with a soft cloth. The waterjacket is again placed so as to surround the ball and the cover put on as before, the circulation of water in the jacket having been started.

It is now only necessary to take readings of both thermometers every half minute. The temperature of the hot water will be practically constant, but it is advisable to take the readings in case of alteration. The calorimeter thermometer may be read till it reaches 20° C.

It will be convenient to explain here the reason for cooling the ball 6° or 7° before starting. In the preceding remarks no notice was taken of the fact that there will be radiation to or from the surface of the ball unless the latter is at the same tempeture as its surroundings. It would be impossible to allow for this by calculation, as the surface is altered before every test by being heated while the wire is being soldered into the ball. For the purpose of getting rid of the necessity of allowing for this radiation, the ball is cooled down.

Let Q_1 = the quantity of heat which flows along the wire in unit time when the hot end is at T[°] and the cool end at $\theta^{°}$ above the temperature t of the air and water-jacket, and let Q_2 = the quantity when the cool end is $\theta^{°}$ below that of the air.

Then, assuming that the conductivity does not change very much through $2\theta^{\circ}$, and that α , the loss by radiation in unit time when the ball is θ° above the air tempera-

ture, is equal to the gain by absorption in unit time when the ball is θ^2 below the air temperature, we have

$$\mathbf{Q}_1 = \frac{\mathbf{K}\mathbf{A}}{l} \left[\mathbf{T} - (t+\theta)\right] - \alpha$$

and

$$Q_2 = \frac{KA}{l} [T - (t - \theta)] + \alpha$$

Therefore

$$\frac{\mathbf{Q}_1 + \mathbf{Q}_2}{2} = \frac{\mathbf{K}\mathbf{A}}{l} \left(\mathbf{T} - t\right).$$

It is seen by the last equation that the effect of radiation to or from the surface of the ball is completely eliminated since the coefficient of emission is numerically equal to the coefficient of absorption for the same difference of temperatures. It therefore fortunately does not matter how the surface of the ball becomes changed, so long as it remains the same during the half hour of the experiment. As a matter of fact, during the soldering process the surface becomes very much tarnished.

Table I. gives a specimen experiment taken at random from my laboratory book.

FRIDAY, 23rd March,	1894.—Pure Silve	er Wire (annealed)	. Length = 6.59	centims.
Diamete	er = 202 centim.	Temperature of A	$Lir = 14.3^{\circ} C.$	

I. Reading taken every half-minute.	II. Temperature of hot end.	I. Reading taken every half-minute.	II. Temperature of hot end.
$^{\circ}$ C. 10·3 10·5 10·75 10·95 11·15 11·35 11·55 11·75 12·15 12·35 12·55 12·55 12·75 12·95 13·1 13·3 13·5 13·65 13·85 14·05 14·25 14·4	$^{\circ}$ C. 98:2 98:2 98:2 98:2 98:3 98:3 98:2 98:3 98:3 98:3 98:2 98:3 98:3 98:2 98:3 98:4 98:3 98:4 98:3 98:4 98:3 98:4 98:4 98:4	$^{\circ}$ C. 14.75 14.9 15.1 15.25 15.45 15.6 15.75 15.9 16.05 16.25 16.4 16.55 16.7 16.85 17.0 17.15 17.3 17.45 17.6 17.7 17.86 18.0	$^{\circ}$ C. 98.3 98.4 98.6 98.5 98.6 98.6 98.6 98.6 98.6 98.6 98.6 98.6
14.6	98·3		90 0

The numbers in column I. are put on a curve, as shown in diagram II. From this curve the rise in temperature in half a minute is read off for x° above the temperature of the air, and this is added to the rise for x° below the temperature of the air, where x is any value from 0 to 5 or 6. In this way as many as 10 or 15 values are obtained. If the curve were quite regular, each of these values would be the same, since they each represent the rise in temperature per minute for the same difference of temperature, but they are found to vary by about 1 or 2 per cent. But, by taking the mean of 10 or 15 values, it will be seen that the result obtained must be very near the correct value for the rise in temperature by the thermal capacity, C, of the ball to find the quantity of heat that has passed along the wire in one minute, and the conductivity can be calculated from the formula

$$\mathbf{K} = \frac{\mathbf{C}\boldsymbol{\theta}l}{\pi r^2 \left(\mathbf{T} - t\right) 60}$$

where r is the radius of the wire.

In order to obtain an accurate determination of the thermal capacity of the ball, I took it to Dublin, where the capacity was most carefully determined for me, during the time I was there, by Dr. JOHN JOLY, F.R.S., by his most ingenious steam calorimeter method.* I have to thank Dr. JOLY for the trouble to which he put himself in making the determination.

As the most important thing in testing the method is to show that with different lengths the resulting determination of the conductivity remains practically the same, these series of tests and the results will be given first.

The wire first used was what was called six years ago high electrical conductivity copper. The diameter was 2.1 millims., density 8.85, volume specific (electrical) resistance, 1834 in electromagnetic units. This wire was almost exclusively used, but in the course of the work tests were made of wire got from Messrs. GLOVER and Co. in the end of the year 1890. Messrs. Glover's wire was found to have considerably higher conductivity, both electrically and thermally, than the firstmentioned wire, which for convenience will be called the laboratory copper, as it was what was used for all the electrical work in the laboratory. Taking the laboratory wire as 100 per cent. conductivity (thermally and electrically), it was found that Messrs. GLOVER's wire was 106.6 per cent. electrical, and 108 per cent. thermal conductivity.

These results will be referred to further on (p. 180). They are merely mentioned here to show that the best conducting wire was not used for the exhaustive tests.

Table II. shows the record of series of experiments made on laboratory copper wire. The wire was soldered into the heating box and ball as described; an experiment was made and the length measured carefully. The ball was then heated by a blow-

* J. JOLY, 'Roy. Soc. Proc.,' vol. 41, p. 352, 1886.

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pipe flame to allow the wire to be taken out. A short piece was then cut off and the shortened wire again soldered into the ball.

TABLE II.—Showing rise of Temperature of Calorimeter Ball with time. Diameter of wire = 210 centim. Temperature readings taken every half-minute.

$\begin{array}{c} \text{Length} \\ = 6.31 \text{ centims.} \end{array}$	$\begin{array}{c} \text{Length} \\ = 5.87 \text{ centims.} \end{array}$	$\begin{array}{c} \text{Length} \\ = 5.23 \text{ C.} \end{array}$	$\begin{array}{c} \text{Length} \\ = 4.39 \text{ centims.} \end{array}$	$\begin{array}{c} \text{Length} \\ = 4.01 \text{ centims.} \end{array}$
Temp. reading at every half-minute.	Temp. reading at every half-minute.	Temp. reading at every half-minute.	Temp. reading at every half-minute.	Temp. reading at every half-minute.
° C. 6·45 6·65 6 85 7·05 7·25 7·45 7·65 7·85 8·05 8·25 8·45 8·65 8·85 9·05 9·2 9·4 9·55 9·75 9·95 10·1 10·3 10·45 10·65 10·85 10·95 11·15 11·3 11·45 11·6 11·8 11·95 12·1 12·25 12·4 12·6 12·75 12·9 13·05	$^{\circ}$ C. $6\cdot 25$ $6\cdot 45$ $6\cdot 7$ $6\cdot 9$ $7\cdot 1$ $7\cdot 3$ $7\cdot 5$ $7\cdot 75$ $7\cdot 95$ $8\cdot 2$ $8\cdot 4$ $8\cdot 6$ $8\cdot 8$ $9\cdot 0$ $9\cdot 2$ $9\cdot 4$ $9\cdot 6$ $9\cdot 8$ $10\cdot 0$ $10\cdot 15$ $10\cdot 35$ $10\cdot 55$ $10\cdot 75$ $10\cdot 9$ $11\cdot 1$ $11\cdot 25$ $11\cdot 45$ $11\cdot 65$ $11\cdot 8$ $12\cdot 0$ $12\cdot 15$ $12\cdot 35$ $12\cdot 55$	° C. 7.0 7.25 7.5 7.75 8.0 8.2 8.4 8.65 8.85 9.1 9.35 9.55 9.8 10.0 10.2 10.4 10.65 11.05 11.25 11.45 11.65 12.1 12.3 12.5 12.7 12.9 13.05 13.25	$^{\circ}$ C. 6.65 6.95 7.2 7.45 7.7 8 0 8.25 8.5 8.75 9.05 9.3 9.6 9.85 10.1 10.35 10.6 10.35 10.6 10.8 10.05 11.3 11.5 11.75 12.0 12.25 12.45 12.7 12.95 13.15 13.35 13.56 13.8 14.0 14.25 14.45	$^{\circ}$ C. 7:35 7:7 8:0 8:3 8:6 8:95 9:25 9:55 9:85 10:15 10:40 10:75 11:05 11:36 11:65 11:9 12:2 12:5 12:75 13:0 13:25 13:5 13:8 14:05 14:3 14:55 14:8 15:85 16:1 16:8 16:55 16:8
Temp. of air 9° 85 C. Temp. of hot water 97° 3 C.	Temp. of air 9°·1 C. Temp. of hot water 97°·0 C.	Temp. of air 10°.0 C. Temp. of hot water 97°.0 C.	Temp. of air 10°·35 C. Temp. of hot water 96·4° C.	Temp. of air 12°·3 C Temp. of hot water 96°·7 C.

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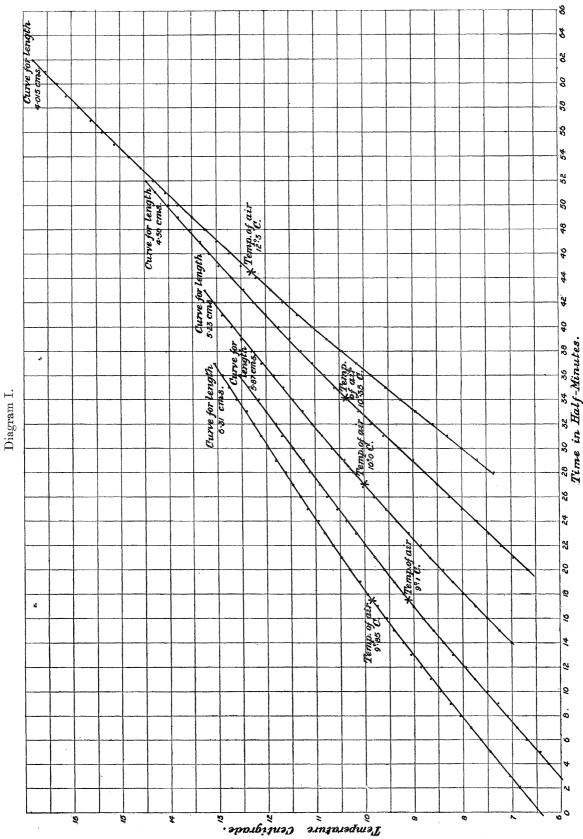




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MR. J. H. GRAY ON A METHOD OF DETERMINING



The temperature of the hot water varied not more than half a degree during an experiment, and the value given in each column of the preceding Table is the mean throughout the time. The columns of temperatures were, immediately after an experiment, put on a curve with time as abscissæ. The effect of radiation to and from the calorimeter ball is fairly well marked. At the point corresponding to the temperature of the air in each curve there is an increase of curvature, caused by the fact that the radiation has changed from negative to positive.

In order to find the flow of heat, the rise of temperature per minute was read from the curve at a temperature x° below that of the air, and this was added to the rise for x° above that of the air. x varied from 0° to 4° or 5° . By this means from ten to fifteen readings were got, and the mean of these gave the rise at the temperature of the air.

For example, for the length 6.31 centims. in the first column of Table I., the rise thus obtained from the curve, Diagram I., was .3605 in one minute. The capacity of the ball and of the part of the thermometer with the water in the hole was found to be 68.9.

There

$$K = \frac{68.9 \times .3605 \times .631}{\pi \times (.105)^2 \times .87.45 \times .60}$$

= .883 C.G.S. unit.

This value is not corrected for the error given by the approximate formula already mentioned.

Error

$$= (\mathbf{V}_1 - \theta) \frac{\frac{a}{2l} \frac{\mathbf{K}}{k} \frac{b-a}{b}}{1 + \frac{a}{2l} \frac{\mathbf{K}}{k} \frac{b-a}{b}}$$

 $\doteq \cdot 69^{\circ}$ in this case.

This makes the difference of temperature less by '7°, and when this correction is made we get for the conductivity '889 C.G.S. unit. The conductivity as calculated from five different lengths becomes, after the correction is made—-

Conductivity.
.889
·893
·890 ·887
.883

The greatest difference between these values is a little over 1 per cent. Taking $2 \land 2$

their mean, we get for the thermal conductivity of the laboratory copper wire \cdot 8884 C.G.S. unit. This value is the mean conductivity between the temperatures 97° C. and 10° C.

The following Table gives the results of a series of tests on another portion of the same wire :----

Length in centims.	Conductivity.
$6.11 \\ 5.71 \\ 4.80 \\ 4.43$	-888 -883 -892 -889

The mean of these values is \cdot 8880, being $\frac{1}{22}$ per cent. less than that obtained from the preceding series.

Taking ÅNGSTRÖM'S formula,

$$\mathbf{K} = 1.027 \ (1 - .00214t),$$

and finding K for 53°, which is the mean of 97° and 10°, we get K = .9208 C.G.S. unit.

The close agreement in the values obtained with different lengths shows that the errors already mentioned as possible are practically eliminated. ÅNGSTRÖM'S value is 4.5 per cent. greater than .8884, but, as has been mentioned (p. 176), the conductivity of the laboratory copper wire is 8 per cent. less than that of GLOVER'S wire afterwards tested. In a previous paper, ÅNGSTRÖM gives .91 as the value for 51.3° C.

In a paper read before the Royal Society last year, Dr. R. W. STEWART, using the Forbes method, but substituting a single thermo-electric junction for the thermometers, gives the values for copper and iron. At the temperature 53° C. he gets for copper K = 1.067, which is 10 per cent. higher than the value obtained for any specimen of copper tested in the present investigation.

The conductivity of the wire obtained from Messrs. GLOVER and SON was found to be 9594 C.G.S. This was the best conducting copper tested by the present method. The specific electrical resistance was 1730 in absolute units.

To test separately the effect of any alterations, separate experiments were made.

I. Instead of enclosing the whole length of the wire (laboratory copper) in a tube, only a part was enclosed.

The paper tube was shortened by 2 or 3 millims. each time, and the conductivity of the same length of wire was determined after each shortening of the tube. The result found was, that the shortening (which was, of course, done from the cool end of the wire) had practically no effect on the value so long as it was arranged that there were no draughts of cold air. If for no other reason, the paper tube is necessary to

prevent draughts, as the latter make a determination impossible. It was found that the paper tube could be shortened as much as to leave the lower half of the wire exposed without any appreciable diminution of the value obtained. When it was shortened much further, the value began to diminish till, when the tube was removed altogether, the value obtained was found to be fully 6 per cent. lower than when the tube completely covered the wire. When the wire was bare it was found very difficult to prevent draughts caused by the hot wire, and these draughts made the readings of the thermometer very irregular.

In connection with this, it will be noted that there is a particular advantage in having the calorimeter ball lower in position than the heating box, as the hot air round the latter rises, and so does not affect the water-jacket. It has been suggested, however, that a separate experiment should be made to test whether any heat reached the ball otherwise than through the wire. For this purpose the ball was suspended by silk threads, in such a way that its highest point was 4.4 centimetres from the bottom of the heating box. The water jacket was placed round the ball, and the sheets of paper put on the top of the jacket. The water in the heating box was kept boiling for twenty-five minutes, and the temperature of the ball, as indicated by the thermometer in it, was noted at intervals. No change in the thermometer reading could be detected, although $\frac{1}{40}$ th of one degree can be read without difficulty on the thermometer scale.

As a further test of the effect of the paper tube, the upper half length of the wire which was being tested, was left unprotected by any tube, while the lower half was enclosed. The result was practically the same as if there had been no tube at all.

In order to make certain that the thermometer in the hot water indicated the temperature of the upper end of the wire, a thermo-electric junction was used. The junction was made of very thin wires of copper and platinoid, and, after being wrapped once round the hot end of the wire just at the end, was soldered there. The other junction was fixed to a thermometer and immersed in water. The heating box was then filled with water, which was kept boiling. The water in the vessel containing the other junction was gradually heated up till there was no deflection in the mirror galvanometer used. Both junctions must then be at the same temperature. When there was no deflection in the galvanometer the thermometers were found to be indicating the same temperatures.

Several qualities of copper were tested, the results of which are given below.

Copper wire, made by Messrs. BOLTON and Co., Cheadle. This wire was by mistake sent away before its electrical conductivity was measured, and it cannot be got again.

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Length used (in centims.).	Mean conductivity between 10° C. and 97° C.
$7.0 \\ 6.33 \\ 5.7 \\ 5.1$	·867 ·862 ·859 ·858

The greatest variation here is 1 per cent., and the mean value is .8612.

Some specimens of copper wire were bought in a plumber's shop, of quality used for bell-hanging.

Specimen.	Diameter (in centims.).	Specific resistance (electrical).	Mean thermal conductivity.
$rac{1}{2}$	·200 ·204	$\begin{array}{c} 5545\\ 4701\end{array}$	$^{+3198}_{-3497}$

Conductivity of Laboratory wire Conductivity of Specimen 1	=	2.78	for heat,
J L		2.86	for electricity.
$\frac{\text{Conductivity of Laboratory wire}}{\text{Conductivity of Specimen 2}}$	=	2.54	for heat,
		2.56	for electricity.
Conductivity of GLOVER's wire Conductivity of Laboratory wire		1.08	for heat,
			for electricity.

In all the wires tested it was found that if one metal was a better conductor for electricity it was also better for heat. This has been noticed by several investigators, notably Professor TAIT, and WIEDEMANN and FRANZ. Beyond this the present results cannot go, as enough trials were not made to allow of comparison. Previous experimenters have found that the ratio of electrical conductivities of two wires is not exactly equal to the ratio of thermal conductivities. This is indeed to be expected, if the coefficients already obtained for the alteration with temperature are accurate. For example, in copper the coefficient of variation per degree for electrical conductivity is very much greater than that found for thermal conductivity, so that, even if the ratios were equal at one temperature, they must be unequal at all other temperatures. In some of the wires tested the electrical and thermal ratios differed by as much as 4 or 5 per cent.

Before the present investigation, the absolute values for the conductivity of the

more expensive metals had not been determined, although relative values had been found by WIEDEMANN and FRANZ.*

I am very much indebted to Messrs. JOHNSON, MATTHEY, and Co. for their great kindness in preparing and lending to me wires of gold, platinum, silver, and other pure metals, of 2 millims. diameter, and of such a length as to enable me to measure without difficulty both the thermal and electrical conductivities.

Unfortunately, I cannot find a record of the value obtained for the electrical conductivity of the gold wire, and it has been returned some time ago. As, however, Messrs. JOHNSON, MATTHEY, and Co. stated, when sending it, that it was as pure as could be made, it will perhaps be sufficient for me to use the value that has already been found for the electrical conductivity of gold as determined by other experimenters.

The curves for the calculation of the conductivity of silver wire are shown in Diagram II. The values for the different lengths are given below.

SILVER Wire.

Length.	Thermal conductivity in C.G.S. units between 15° C. and 98° C.
$7.86 \\ 6.59 \\ 6.59 \\ 5.61$	·956 ·960 ·963 ·973

It will be observed that the second and third values, although for the same length, differ by about $\frac{1}{3}$ per cent. They are both given however, as they agree within the limits of observational errors. The mean of these values is '9628.

As the curves for gold and platinum are very similar to those for copper and silver, it may be enough to give the values obtained for their conductivities.

GOLD Wire (not annealed). Diameter = 202 centim.

Thermal conductivity in C.G.S. unit.	Electrical resistance as determined by Dr. MATTHIESSEN.
·7464	2188

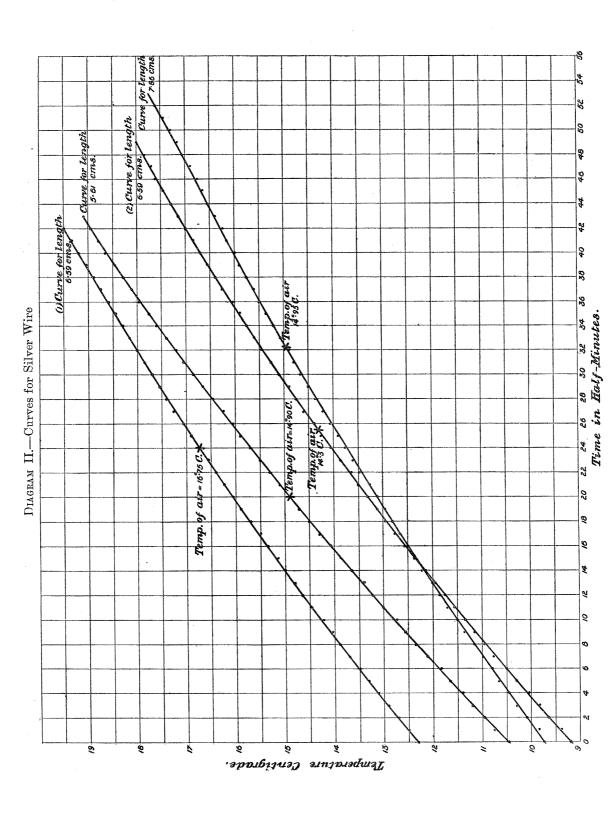
Comparing these values with those for Messrs. GLOVER's copper, which was found to be '959, we find that the thermal conductivity of gold is 78 per cent. and the electrical conductivity 81.6 per cent. that of copper.

* 'Annales de Chemie,' vol. 41, p. 107, 1854.



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PLATINUM Wire (not annealed). Diameter = $\cdot 202$ centim.

Thermal conductivity.	Electrical resistance.
·1861	9180

Here the thermal and electrical conductivities are each 19 per cent. of the conductivity of copper.

The gold, platinum, and silver were afterwards carefully annealed by Messrs. JOHNSON, MATTHEY, and Co., and the conductivities again determined. In each of the cases the alteration due to annealing was less than 1 per cent. both in electrical and thermal conductivity.

The results for the different metals are therefore—

MEAN Conductivity between Temperatures 10° C. and 97° C.

									Diameter.
Copper—Specim " Very { " impure { " Silver Gold Platinum	en 1 2 3 4 5 	• • • • • • • •	· · · · · · ·	• • • •	•	• • • •	•	9594 8884 8612 3497 3198 9628 7464 1861	$\begin{array}{c} \text{millims.} \\ 2 \cdot 00 \\ 2 \cdot 11 \\ 3 \cdot 09 \\ 2 \cdot 04 \\ 2 \cdot 04 \\ 2 \cdot 04 \\ 2 \cdot 02 \\ 2 \cdot 00 \\ 2 \cdot 00 \\ 2 \cdot 00 \end{array}$

It is intended to use other liquids than boiling water to heat one end of the wire, and in this way test the alteration of conductivity with temperature. Up to the present time no alloys have been tested, but it is intended that tests should be made of some, such as platinoid and German silver; also iron, as pure as possible, might be tested.

Instead of boiling water, steam was used for some time in this investigation, and was in some respects found to be more convenient. Fig. 7 is a sketch showing a section through the middle of the apparatus.

The steam is generated in the vessel W, passes along the upper tube T in the direction of the arrows, and blows directly on the end of the wire, afterwards passing out through the outside copper tube P, and escaping by the outlet B.

The thermometer D indicates the temperature of the steam just when it strikes the wire. It will be seen that the outer tube with the steam in it serves as a steam jacket, and thus keeps the steam in the inner tube T at a high temperature. The sloping bottom where the wire is fixed at A is so made to prevent water accumulating there. To ensure that as much steam as will supply all the heat that the copper can take up is impinging a. A, it is only necessary to arrange that the steam emerges at B as steam.

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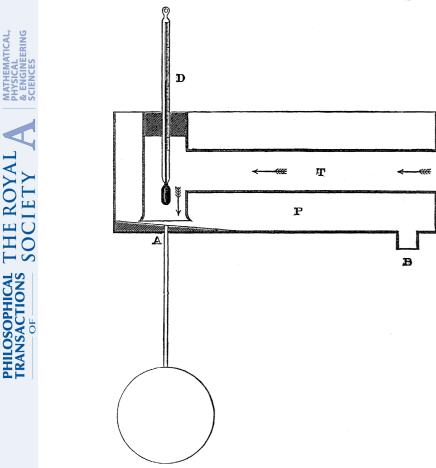


Fig. 7.

The outside tube need not be more than 4 centims. diameter, and may be round, but the part where the wire is soldered in must be thickened and made as shown in the sketch, so that there may be no risk of water gathering above the wire. The length of the tube need not exceed 15 centims. This allows sufficient length for the tube to be inserted into the screen, which prevents the heat of the lamp from altering the temperature of the ball. The diameter of the inside tube may be 1.5 centims. With this apparatus most satisfactory results were obtained.

w

When a metal is tested for the first time, it will be advisable to find its approximate thermal conductivity by comparing its electrical conductivity with copper. This will give an idea as to which calorimeter ball to use, and what length of wire will give a convenient rise of temperature per minute. A test is then almost as simple as for electrical conductivity.