On the Thermal Conductivities of Single and Mixed Solids and Liquids and their Variation with Temperature

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X. *On the Thermal Conductivities of Single and Mixed Solids and Liquids and their Variation with Temperature.*

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PART I. CONDUCTIVITIES AND TEMPERATURE COEFFICIENTS OF SOLIDS.

Sketch of Method.

IN determining thermal conductivities* of solids not very good conductors of heat, the method least open to objection on theoretical grounds is the one in which a spherical shell of the substance to be tested is filled with, and the exterior surrounded by, some good conductor of heat, the temperatures of the conductors, inside and out, being observed by means of thermometers or thermo-junctions, and maintained constant by heat supplied, *e.g.*, electrically, to the inner conductor at a measured rate (fig. 1). Difficulties, mainly of a mechanical kind, present themselves, however, in the carrying out of this method, which render it advisable to sacrifice some of the theoretical simplicity, in order to make the method more practicable.

Fig. 1.

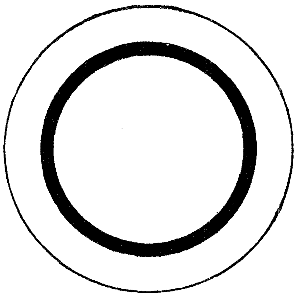


Fig. 2.

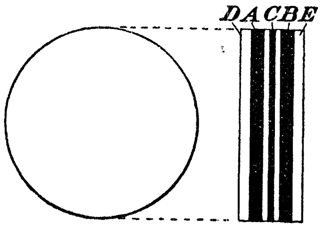
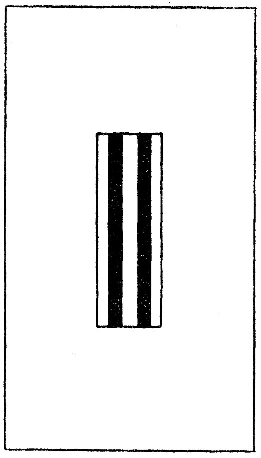


Fig. 3.



These difficulties are overcome most easily by having the material to be tested, the conductor to which heat is supplied, and the outside conductors, in the form of flat circular discs of the same diameter (fig. 2), the good-conducting disc, *C*, to which heat

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* The extremely good account of previous methods and results given by GRAETZ in WINKELMANN'S 'Handbuch der Physik,' vol. 2, pp. 273–314, renders an account of such work unnecessary here.

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is supplied, being placed between two discs of the material to be tested, *A* and *B*, and two other good-conducting discs, *D* and *E*, placed in contact with the outer surfaces. By placing thermo-junctions in each good-conducting disc we can determine the relation between the heat supplied to the inner disc and the differences of temperature between the inner and outer discs.

If all the heat supplied to the inner disc flowed through the substance to be tested to the outer discs, the thermal conductivity of the material would be thus determined, but some heat is lost from the curved surfaces of the discs by conduction and radiation through the air to the enclosure in which the discs are placed. The amount thus lost can be determined by observing the temperature of the enclosure, if the loss per square centimetre per degree excess of temperature of the edges of the discs over the inside of the enclosure were known.

To enable this quantity to be determined directly by experiment, the whole of the heat supplied to the discs must be lost in the same way, *i.e.*, by conduction and radiation through air, and to satisfy this condition, the collection of discs should be placed in the centre of an air bath kept at constant temperature (fig. 3). The heat lost from the curved surfaces of the discs then follows with sufficient closeness the same law as that lost from the flat surfaces of the outer discs, and the relative amounts of the two can be determined from a knowledge of the areas and temperatures of the various surfaces, if the surfaces have the same "outer conductivity" or "emissivity," an equality which is easily secured by varnishing them.

Once the method of surrounding the discs by an enclosure at constant temperature has been adopted, a further simplification of the arrangement of discs is possible. If one of the discs of the substance under test and one of the outer discs were removed, the relative amounts of heat lost by the heating disc, *C* (fig. 4), by conduction and radiation directly to the air from its exposed surfaces, and by conduction through the disc, *B*, of material experimented on, partly to the air directly by conduction and radiation from the surface of *B*, and partly by conduction to the outer good-conducting disc, *E*, and radiation from its surfaces, could still be calculated, and, the total heat supplied being known, the conductivity of the material determined. On account of this method requiring only one disc of a substance the conductivity of which is to be determined, it has been adopted in the experiments to be described.

Description of Apparatus.

The materials to be tested were cut into discs of 4 centims. diameter, and of various thicknesses, in order to make the magnitude of the difference of temperature of the two flat surfaces, suitable for observation with the thermo-junctions employed. The discs between which the material was placed were of copper, and had the same diameter. On one side of the substance to be tested was placed a single copper disc, *M* (fig. 5), ·320 centims. thick, on the other side a compound disc, consisting of two discs of copper, *C*, ·103 centim., and *U*, ·312 centim. thick, with a flat heating coil of double silk-covered No. 25 platinoid wire, *P*, between them, well insulated by means of mica and shellac, the total thickness of the coil and mica being ·110 centim. The contacts between the surfaces of the copper discs *U* and *M*, and the substances, were improved by smearing them with glycerine and sliding them together. The glycerine was generally sufficient to keep the discs together during an experiment, but to ensure the surfaces remaining properly in contact, a few turns of silk thread were wound round the discs.

At opposite extremities of a diameter of each disc, two holes, ·7 millim. diameter and 3 millim. deep, were bored towards the centre of the disc, and into one hole of each disc a platinoid, and into the other hole a copper, wire was soldered. The wires were double silk covered, about 30 centims. long, and were all cut from the same two coils.

Fig. 4.

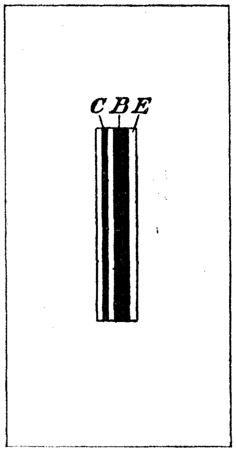


Fig. 5.

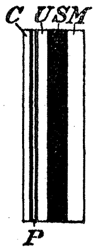


Fig. 6.

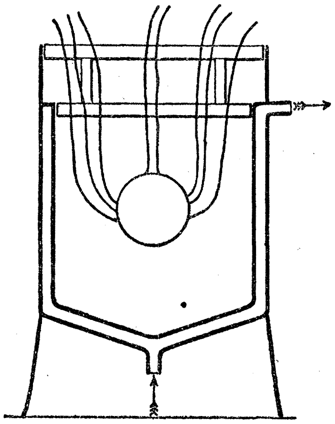
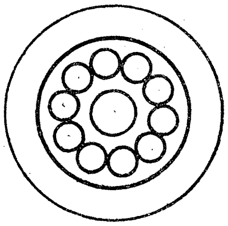


Fig. 7.



The surfaces of the pile of discs were varnished to give them the same emissivity, and the pile placed in the centre of a double-walled air-bath (fig. 6), of 17 centims. height, 15 centims. length, and 7 centims. breadth, supported on legs about 4 centims. above the table. The top of this bath consisted of a double wooden lid, cut down the centre to allow the wires from the discs to pass out. The edges of the lid were covered with green baize, in which the wires embedded themselves, and which closed the bath sufficiently to prevent convection currents between the inside and outside. On the outer walls of the air-bath a coil of insulated platinoid wire was wound, and an electric current could be sent through the wire to keep the bath at any required temperature. The inner walls were about 1 centim. within the outer, and between the two water could be circulated, or the space could be filled with air simply. A thermo-junction was soldered to the centre of an inner surface, and enabled the temperature of the enclosure to be determined. The wires from the heating coil, *P*, after passing out through the lid, dipped into mercury cups, from which wires passed to the cells supplying the heating current, the power absorbed being regulated by a rheostat and measured by a wattmeter.

Each of the thermo-junction wires was brought to a mercury cup, made by cutting 4 centim. lengths from a piece of thin glass tubing with a bore of about 3 millims., sealing one end of each length, and fastening it, with the sealed end down, in a brass tube 5 centims. long and 3 centims. in diameter, mounted in a block of wood and containing mercury. Ten of these glass tubes nearly full of mercury were arranged in a circle round the bulb of a thermometer graduated in $\frac{1}{10}$ degrees, which was placed in the centre of the brass tube. To diminish loss or gain of heat, the brass tube was wrapped with green baize (fig. 7). The ends of the wires leading to the potentiometer arrangement for measuring the electromotive force in the thermo-electric circuits, could be placed in any two of these mercury cups, and by means of an additional short wire of platinoid, any two thermo-circuits could be placed in series, and the difference of the electromotive forces in the two determined.

Theory of Flow of Heat in Discs.

Let H = heat generated per second in the heating coil.

h = heat lost per second, per square centimetre per degree excess of temperature of the discs over that of the enclosure.

v = excess of temperature over that of enclosure.

t = actual thickness of a disc, plus a small correction, p. (409) to allow for heat lost along thermo-wires.

r = radius of discs.

Subscripts C, U, M, S refer to "cover" "upper" "middle" discs,* and disc of substance respectively, the heating coil coming between C and U, and the substance to be tested between U and M (fig. 5).

When the "steady state" has been attained, the heat received per second by the copper disc M from the disc of substance S, and given up to the air

$$= \pi r^2 h \left(1 + \frac{2t_M}{r}\right) v_M.$$

Similarly, the heat received by the disc S, of material tested and given up to the air and to the disc M

$$= \pi r^2 h \left(1 + \frac{2t_M}{r}\right) v_M + \pi r^2 h \frac{2t_S}{r} \cdot \frac{v_M + v_U}{2}.$$

If k is the thermal conductivity of the material, the heat flowing through the disc tested

$$= \pi r^2 k \frac{v_U - v_M}{t_S}.$$

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* The reason for the choice of these terms will be understood from Part II.

Hence we have, to a very close degree of approximation,*

$$k\,\frac{v_{\mathrm{U}} - v_{\mathrm{M}}}{t_{\mathrm{S}}} = h\left\{v_{\mathrm{M}} + \frac{2}{r}\left(\overline{t_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{4}}\,v_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{4}\,v_{\mathrm{U}}\right)\right\}.$$

The total heat imparted to the discs and lost from their surfaces

$$= \mathrm{H} = \pi r^2 h\left\{v_{\mathrm{M}} + v_{\mathrm{C}} + \frac{2}{r}\left(t_{\mathrm{M}}v_{\mathrm{M}} + t_{\mathrm{S}}\,\frac{v_{\mathrm{M}} + v_{\mathrm{U}}}{2} + t_{\mathrm{U}}v_{\mathrm{U}} + t_{\mathrm{C}}v_{\mathrm{C}}\right)\right\}.$$

Eliminating h between these equations we have

$$k = \mathrm{H}\,\frac{\left(1 + \frac{2}{r}\,\overline{t_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{4}}\right)v_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{4}\,v_{\mathrm{U}}}{\left(1 + \frac{2}{r}\,\overline{t_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{2}}\right)v_{\mathrm{M}} + \left(1 + \frac{2}{r}\,t_{\mathrm{C}}\right)v_{\mathrm{C}} + \frac{2}{r}\left(t_{\mathrm{U}} + \frac{t_{\mathrm{S}}}{2}\right)v_{\mathrm{U}}}\cdot\frac{t_{\mathrm{S}}}{\pi r^2\,(v_{\mathrm{U}} - v_{\mathrm{M}})},$$

and from the second equation we have

$$h = \frac{\mathrm{H}}{\pi r^2\left\{\left(1 + \frac{2}{r}\,\overline{t_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{2}}\right)v_{\mathrm{M}} + \left(1 + \frac{2}{r}\,t_{\mathrm{C}}\right)v_{\mathrm{C}} + \frac{2}{r}\left(t_{\mathrm{U}} + \frac{t_{\mathrm{S}}}{2}\right)v_{\mathrm{U}}\right\}},$$

which will enable us to determine k and h from observations of H and the temperatures of the discs.

In the foregoing theory it has been assumed that the steady state of temperature distribution had been attained. As, however, an infinite time is required before this condition is satisfied, it remains to determine at what previous period observations may be taken without the results deduced from these observations being in error by say $\frac{1}{4}$ per cent.

If the temperature of the "middle disc" is increasing at a rate dv_{M}/dt, the expression for the heat it receives becomes

$$\pi r^2 h\left(1 + \frac{2t_{\mathrm{M}}}{r}\right)v_{\mathrm{M}} + m_{\mathrm{M}}c_{\mathrm{M}}\,\frac{dv_{\mathrm{M}}}{dt}$$

where m_{M} is the mass, and c_{M} the specific heat of the material, of the disc.

Similarly, the expression for the heat received by the disc of substance, since we may assume that the discs increase in temperature at the same rate dv/dt, becomes

$$\pi r^2 h\left(1 + \frac{2t_{\mathrm{M}}}{r}\right)v_{\mathrm{M}} + \pi r^2 h\,\frac{2t_{\mathrm{S}}}{r}\cdot\frac{v_{\mathrm{M}} + v_{\mathrm{U}}}{2} + (m_{\mathrm{M}}c_{\mathrm{M}} + m_{\mathrm{S}}c_{\mathrm{S}})\,\frac{dv}{dt}\;.$$

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* It will be noticed that the heat flowing through the substance has been taken equal to the mean of the heats flowing into and out of it respectively. The closeness of this approximation may be tested by using the values of v in terms of x, obtained on the usual assumption of plane-isothermal surfaces, *i.e.*,

$$v = \mathrm{A}\cosh \alpha x + \mathrm{B}\sinh \alpha x.$$

Hence,

$$\pi r^2 k \frac{v_U - v_M}{t_S} = \pi r^2 h \left\{ v_M + \frac{2}{r}\left(t_M + \frac{t_S}{4}\right) v_M + \frac{t_S}{4} v_U \right\} + \left(m_M c_M + \frac{m_S c_S}{2}\right) \frac{dv}{dt},$$

and the total heat imparted to the discs

$$= H = \pi r^2 h \left\{ v_M + v_C + \frac{2}{r}\left(t_M v_M + t_S \frac{v_M + v_U}{2} + t_U v_U + t_C v_C\right)\right\} + \frac{dv}{dt} \Sigma mc.$$

Eliminating h between these equations, we have

$$\pi r^2 k \frac{v_U - v_M}{t_S} - \left(m_M c_M + \frac{m_S c_S}{2}\right) \frac{dv}{dt}$$

$$= \left(H - \frac{dv}{dt} \Sigma mc\right) \frac{\left(1 + \frac{2}{r} \overline{t_M + \frac{t_S}{4}}\right) v_M + \frac{t_S}{4} v_U}{\left(1 + \frac{2}{r} t_M + \frac{t_S}{2}\right) v_M + \left(1 + \frac{2}{r} t_C\right) v_C + \frac{2}{r}\left(t_U + \frac{t_S}{2}\right) v_U}.$$

For the discs used $m_M c_M = 3{\cdot}2$, $m_S c_S = 1{\cdot}8$, $\Sigma mc = 11{\cdot}5$, and during the experiments H was about ·22, and the value of the fraction on the right-hand side of the equation, ·4. Hence, for the error introduced by neglecting dv/dt to be less than $\frac{1}{4}$ per cent., we must have

$$(-4{\cdot}1 + 4{\cdot}6) \frac{dv}{dt} < \frac{{\cdot}09}{400},$$

or

$$dv/dt < {\cdot}00045,$$

so the change of temperature in 1 minute ought not to exceed ·03° C.

No observations in which this rate was exceeded have been used in what follows.

Loss of Heat along Thermo-Wires.

In the above theory, the heat conducted away from the discs by the wires of the thermo-junctions, has been taken into account by adding a small correction to the thickness of the discs. To determine the amount of this correction for any wire, we write

$$v = v_0 e^{-\sqrt{\frac{ph}{qk}} \cdot x}$$

where v is the temperature excess at a point of the wire distant x from the disc,

p = perimeter of section of the wire.
q = area ,, ,, ,,
k = conductivity of the wire.
h = emissivity ,,

The heat conducted away by the wire per second

$$= - qk\frac{dv}{dx}, \text{ for } x = 0,$$
$$= \sqrt{qk \,.\, ph} \,.\, v_0.$$

For the copper wire used (No. 28), $p = {\cdot}15$, allowing for silk covering; $h = {\cdot}0003$, $q = {\cdot}0011$, and $k = 1{\cdot}0$, therefore

$$\sqrt{qk \,.\, ph} = 2{\cdot}2 \times 10^{-4}.$$

For the platinoid wire, which had the same diameter, we have $k = {\cdot}08$, and

$$\sqrt{qk.ph} = {\cdot}6 \times 10^{-4},$$

therefore total loss of heat along thermo-wires from one disc per second

$$= 2{\cdot}8 \times 10^{-4} \,.\, v_0.$$

If w is the thickness of a disc which would lose the same amount of heat from its edges, we have, since the loss of heat from such a disc $= 2\pi rwhv_0$,

$$w = \frac{2{\cdot}8 \times 10^{-4}}{2\pi rh} = \frac{2{\cdot}8 \times 10^{-4}}{12{\cdot}6 \times 3 \times 10^{-4}} = {\cdot}075 \text{ centims},$$

and the loss along the thermo-wires may be taken into account in the theory of flow of heat in the discs, by taking as the thickness in the formula, p. 403, the measured thickness of the disc plus this quantity.

Constants of the Discs.

$r = 2$ centims., therefore $\pi r^2 = 12{\cdot}5$ sq. centims.

$w = {\cdot}075$ centims.

$t_M = {\cdot}32 + {\cdot}075 = {\cdot}395$ centims., therefore $1 + \frac{2}{r}\overline{t_M + \frac{t_S}{4}} = 1{\cdot}395 + \frac{t_S}{4}$.

$t_C = {\cdot}103 + {\cdot}075 + {\cdot}055^* = {\cdot}233$ centims., therefore $1 + \frac{2}{r}t_C = 1{\cdot}233$.

$t_U = {\cdot}312 + {\cdot}075 + {\cdot}055^* = {\cdot}442$ centims., therefore $\frac{2}{r}\overline{t_U + \frac{t_S}{2}} = {\cdot}442 + \frac{t_S}{2}$.

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* Half the thickness of the heating coil and mica insulation is added to the upper disc and half to the cover.

Hence the formulæ, p. 403, become

$$k = \mathrm{H}\,.\,\frac{\overline{1\cdot395 + \frac{t_{\mathrm{S}}}{4}}\,v_{\mathrm{M}} + \frac{t_{\mathrm{S}}}{4}\,v_{\mathrm{U}}}{\overline{1\cdot395 + \frac{t_{\mathrm{S}}}{2}}\,v_{\mathrm{M}} + 1\cdot233v_{\mathrm{C}} + \overline{\cdot442 + \frac{t_{\mathrm{S}}}{2}}\,.\,v_{\mathrm{U}}} \cdot \frac{t_{\mathrm{S}}}{12\cdot5\overline{v_{\mathrm{U}} - v_{\mathrm{M}}}}.$$

$$h = \frac{\mathrm{H}}{\overline{1\cdot395 + \frac{t_{\mathrm{S}}}{2}}\,v_{\mathrm{M}} + 1\cdot233v_{\mathrm{C}} + \overline{\cdot442 + \frac{t_{\mathrm{S}}}{2}}\,.\,v_{\mathrm{U}}} \cdot \frac{1}{12\cdot5}{}^{*}.$$

Measurement of Power.

The power given to the heating coil of the discs was measured by means of a wattmeter, with its series coils in the main circuit, and the terminals of its shunt coil dipping into the same mercury cups as the terminals of the heating coil. The shunt coil had a resistance of 12 ohms, and was suspended bifilarly by means of the two leading wires. The instrument was standardised by sending a current through a 2-ohm resistance coil of thick platinoid wire, and regulating the strength of this current till the electromotive force at the terminals of the resistance was equal to that of a Clark cell. The wattmeter readings were taken by reversing the connections of the suspended coil to the heating coil in which power was to be measured. The series coils were placed parallel to the magnetic meridian, so that the effect of the earth field on the deflection would be small, and there would be no necessity for reversing the current in the heating circuit. For convenience in working out results approximately, the resistance in series with the suspended coil (320 ohms) was adjusted till the wattmeter deflection was nearly 1000 divisions per gram degree[†] of heat, generated per second in the heating coil.

If H is the heat generated per second in a coil of resistance R, and d is the deflection on the wattmeter, the shunt coil of which has a resistance of r ohms, we have

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[*] The value of h is only required in this work to make certain small corrections in the course of the calculation, and the above equation will not be further referred to. The mean values of h found during the course of the work, are :—

Mean temperature of discs and enclosure.	h.
24° C.	·000276
54	316
72	339

[†] Water gram degree at 15° C. = 4·20 joules.

$$H = K \, . \, d \, . \, \frac{r}{R + r}$$

where K is a constant.

In one of the standardisation experiments the Clark cell had a temperature of 19° C. and an E.M.F. of 1·428 volts. The deflection on the wattmeter was found to be 245·5. Hence, since $R = 2{\cdot}018$, $r = 332$ ohms, we have

$$K = \frac{(1{\cdot}428)^2}{2{\cdot}018 \times 4{\cdot}2} \cdot \frac{1}{245{\cdot}5} \cdot \frac{334}{332} = {\cdot}000986.$$

When, therefore, the wattmeter was connected to the heating coil of the discs, which had a resistance of 3·3 ohms,

$$H = {\cdot}000986 \, \frac{332}{335{\cdot}3} \, . \, d = {\cdot}000976 \, . \, d,$$

from which the heat generated in the coil could be found from the wattmeter deflection.

The power thus measured is that spent in the heating coil and the connections leading to it. A portion only of this power is imparted to the discs themselves, the rest is spent in the short lengths (1·6 centim.) of the platinoid wire projecting outside the discs, and in the No. 22 copper wires leading to the mercury cups outside the air-bath. The total length of the platinoid wire was 150 centims., and 3·2 centims. of it, and 50 centims. of No. 22 copper wire, were outside the discs. The resistance of the coil and connection was 3·3 ohms, ·02 ohms being due to the copper, and ·07 ohms to the projecting platinoid wire. Of the total power generated, therefore, only 321/33.0 = ·973 is imparted directly to the discs.

There is, however, an indirect method by which some of the remaining power may be communicated to the discs, *i.e.*, by thermal conduction along the coil wire, and to determine the amount of this, we require to know the distribution of temperature along the wire.

Assuming that the isothermal surfaces in the wire are planes perpendicular to the axis, we have for the "steady state"

$$qk \frac{d^2v}{dx^2} + w = ph \, . \, v,$$

where

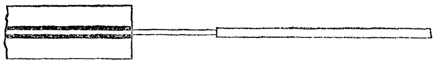
q = cross section of wire,
p = perimeter of wire,
k = conductivity of wire,
h = emissivity of wire,
w = heat developed in 1 centim. length of wire,
v = temperature excess over air, at a point distant x from the junction of the platinoid and copper wires.

The solution of this equation is

$$v - \frac{w}{ph} = \mathrm{A}e^{\sqrt{\frac{ph}{qk}}\cdot x} + \mathrm{B}e^{-\sqrt{\frac{ph}{qk}}\cdot x}$$

where A and B are constants of integration.

Fig. 8.



For the platinoid wire, $w = {\cdot}21/150 = {\cdot}0014$, $p = {\cdot}027$, $h = {\cdot}0003$, $q = {\cdot}002$, $k = {\cdot}08$, therefore

$$\frac{w}{ph} = 170 \text{ and } \sqrt{\frac{ph}{qk}} = {\cdot}22.$$

Hence in the platinoid wire

$$v_1 - 170 = \mathrm{A}_1 e^{\cdot 22x} + \mathrm{B}_1 e^{-\cdot 22x}.$$

For the copper wire, $w = {\cdot}0014/40$, $p = {\cdot}029$, $h = {\cdot}0003$, $q = {\cdot}004$, $k = 1$, therefore,

$$\frac{w}{ph} = 4 \text{ and } \sqrt{\frac{ph}{qk}} = {\cdot}047.$$

Since the temperature of the copper wire to the right is nowhere infinite, we have in the copper wire

$$v_2 - 4 = \mathrm{B}_2 e^{-\cdot 047x}$$

where B_2 is a constant of integration.

When $x = -1{\cdot}6$ in the expression for the temperature of the platinoid wire, the temperature excess v_1 should be equal to that of the discs, which, on the average was 17° C.

Hence,

$$-153 = \mathrm{A}_1 e^{-\cdot 35} + \mathrm{B}_1 e^{+\cdot 35} = {\cdot}705\mathrm{A}_1 + 1{\cdot}42\mathrm{B}_1.$$

Also at $x = 0$ the temperatures and fluxes in the two wires are alike.

Therefore,

$$170 + \mathrm{A}_1 + \mathrm{B}_1 = 4 + \mathrm{B}_2$$

$$\text{and } 35\,(\mathrm{A}_1 - \mathrm{B}_1) = -190\mathrm{B}_2.$$

These three equations determine A_1, B_1, B_2, and give for the temperature in the platinoid wire,

$$v_1 - 170 = -100e^{\cdot 22x} - 57{\cdot}8e^{-\cdot 22x}.$$

The heat flowing per second from the wire to the discs at $x = -1{\cdot}6$

$$
\begin{aligned}
&= qk{\cdot}22\,(-\,100e^{-{\cdot}35} + 57{\cdot}8e^{+{\cdot}35}) \\
&= {\cdot}00016 \times {\cdot}22\,(-\,\overline{100 \times {\cdot}705} + \overline{57{\cdot}8 \times 1{\cdot}42}) \\
&= {\cdot}000035\,(-\,70{\cdot}5 + 82{\cdot}1) \\
&= {\cdot}0004 \text{ gram degrees.*}
\end{aligned}
$$

Hence, ·0008 gram degrees of heat flow per second along the two wires to the discs.

Of the ·21 gram degrees of heat imparted in the coil ·21 × ·027 = ·0057 is expended outside the discs, and of this ·0008 is conveyed to the discs by conduction, leaving ·0049, or about 2·4 per cent., which does not reach the discs. The wattmeter readings must therefore be diminished by this amount to give the power actually imparted to the discs.

Combining this result with the one previously found, we have for the heat, H, imparted to the discs,

$$\text{H} = {\cdot}000953\, d,$$

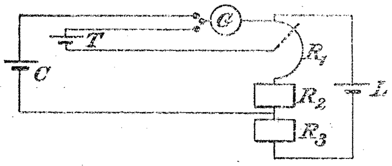
when d is the deflection on the wattmeter.

The Thermo-electric Measurements.

The principle adopted in measuring the electromotive forces in the various thermo-electric circuits, was that of balancing them against the fall of potential down a high resistance in series with a cell of known electromotive force.

The arrangements of the circuits will be understood from the accompanying diagram.

Fig. 9.



R_1, R_2, and R_3 are resistances in series with the Leclanché cell, L. R_2 and R_3 are resistance boxes of platinoid, of 30,000 ohms and 10,000 ohms respectively. R_3 is adjustable, and it was varied until the fall of potential down the 30,000 ohms was equal to that of a Clark cell, C. This adjustment was not absolutely necessary, but was carried out for convenience by the arrangement shown in the figure. The thermo-couple, T, is balanced against the fall of potential down a part of R_1, which represents three dial resistances of copper wire, only one of which is shown in the figure. The movable arms of the dials consisted of short thick copper wires dipping into mercury cups. The dials read respectively, ohms, ·1 ohms, and ·01 ohms. They were made

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[*] More generally the heat conducted along one wire to the discs = ·0077H − ·000071v, where H is the heat generated in the coil, and v the temperature excess of the discs.

of copper wire to get rid of thermo-electric forces in the circuit, *T*, other than those to be measured.

The galvanometer enabled the determinations to be made to about ·003 ohm. By means of the mercury cups (fig. 7) any one of the thermo-electric circuits could be connected through the galvanometer to R_1, and the electromotive force in it determined, or by arranging two of the circuits in opposition, the difference of electromotive forces in any pair could be found.

Standardisation of Thermo-couples.

To determine the constants of each of the thermo-couples, the various copper discs were bound together by tape, a thin sheet of mica being placed between each disc for insulation, and the bulb of a thermometer graduated in $\frac{1}{10}$ degrees was placed in contact with, and bound to, the discs by a few turns of the same tape. The combination was then placed in its usual position in the air bath, and the bath heated by sending a current through the coil encircling it. When the temperature of the bath had been raised to about 50° C., the current round it was diminished till the temperature ceased to rise, and further adjusted till the temperature remained constant. After about half-an-hour the indications of the thermometer in the bath, and of a similar thermometer in the mercury cups in which the other junctions were placed, were read, the electromotive forces in each thermo-circuit found, and the thermometers again read. After a few minutes' interval the process was repeated.

Since in the test of conductivity it is the difference of the temperatures of the discs which is required, observations of differences of the electromotive forces in the various circuits were in each case taken. As these differences were small, and could be observed with the same degree of accuracy as the actual electromotive forces, which were comparatively large, the calculations of conductivity have all been based on them, one of the observations of actual electromotive force having been used to fix the mean temperature of the disc experimented on.

The following table gives the results of the observations :—

θ = the temperature of the discs in the bath.

θ_0 = that of the mercury cups.

U = the number of ohms of the potentiometer necessary to give a balance in the circuit from the "upper disc." 1 ohm corresponds to 1·434/30,000 = ·000044 volt.

U − M = the ohms giving a balance when "upper" and "middle" circuits were opposed.

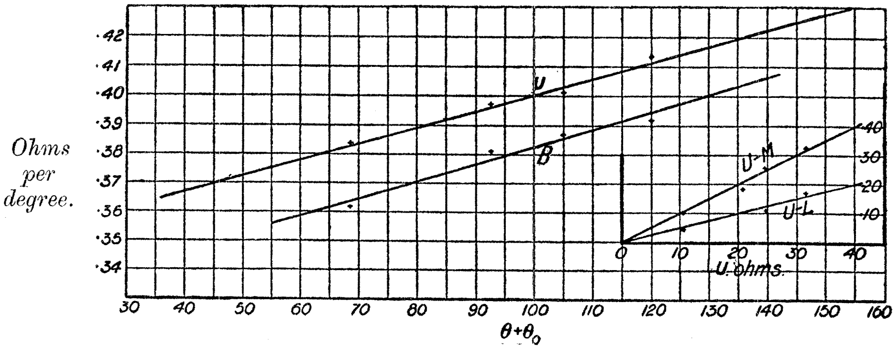
U − L = ditto . . . ditto, when "upper" and "lower" opposed.

B = ditto . . . ditto, when thermo-junction from inside surface of air bath was in circuit.

For convenience of interpolation the numbers headed "ohms per degree" are taken as ordinates, and $\theta + \theta_0$ as abscissæ, of the curves which follow the table.

CONSTANTS of Thermo-junctions.

θ.	θ_0.	Ohms.				Divisors. Ohms per degree.		$\theta + \theta_0$.
		U.	U − M.	U − L.	B.	U.	B.	
47·68°	20·80°	10·31	0·10	0·05	9·72	0·384	0·362	68·5°
47·57	20·91	10·21	0·10	0·04	9·67	0·383	0·362	68·5
82·63	21·75	24·46	0·26	0 12	..	0·402	..	104·9
83·13	21·87	24·67	0·24	0·10	23·73	0·402	0·387	104·9
97·63	21·87	31·34	0·31	0·16	..	0·414	..	119·5
97·63	21·88	31·34	0·32	0·17	29·70	0·414	0·392	119·5
72·60	19·92	20·91	0·18	..	20·05	0·397	0·381	92·5
72·66	19·41	21·15	0·19	..	20·26	0·397	0·381	92·1



It will be noticed from the table that although the wires used for the thermo-junctions were cut from the same bobbins and treated alike subsequently, the thermo-circuits had different constants, the difference in the case of the upper and middle circuits amounting to 1 per cent., and in the case of the upper and heater circuits to 6 per cent.

This prevents the difference of the temperatures of two junctions being determined directly by dividing the electromotive force in circuit when the junctions are placed in series, by a constant. The method to be used is indicated subsequently.

The "cover" and "upper" circuits were found to give identical results, and the upper junction was therefore adopted as the standard, and the differences between its electromotive force and those of the other junctions determined in each case.

To determine the temperature of the junction in the upper disc, given the temperature of the junction in the mercury cups, and the electromotive force in the circuit, we require to divide this electromotive force by a quantity which itself varies to a small extent with the temperature required. If, however, this temperature is known approximately, the value of the divisor may be found from the upper of the preceding curves, and the temperature found more accurately. If necessary this new value of the temperature may be used to find the divisor more accurately, and from it a second approximation to the temperature.

To obviate the necessity of determining the temperature of the disc in this way by two stages, a table of divisors was constructed having a double entry, one, the temperature of the junction at the mercury cups, the other the resistance of the potentiometer for a balance. The form of the table will be seen from the part of it given below :—

Resistance.	Temperature of mercury cups.			
	16°.	17°.	18°.	19°.
Ohms. 1	·365	·366	·367	·368
2	·367	·368	·369	·370
3	·368	·369	·370	·371
..	..	..	..	..
16	·386	·387	·388	·390
17	·387	·388	·390	·391
18	·389	·390	·391	·392

To determine the temperature of the upper junction when the junction in the mercury cups had a temperature of say 18° C., and the resistance for a balance was say 3 ohms, we find from the table that the divisor is ·388, and the temperature difference between the junctions is 3/·388 = 7·73, and the temperature required therefore = 25·73° C.

The same plan was adopted for the junction in the air bath.

Theory of Observations with Thermo-junctions in Series.

If two homogeneous wires of materials a and b have their ends soldered together, and the two junctions are kept at temperatures θ_1 and θ_0, the electromotive force E_1 in the circuit is given by an equation of the form

$$E_1 = (\theta_1 - \theta_0)\, e\, (1 + f\, \overline{\theta_1 + \theta_0})$$

where e and f are constants.

If the junctions of a second pair of materials, a' and b, where a' differs slightly from a in thermo-electric properties, are kept at temperatures θ_2 and θ_0, we have

$$E_2 = (\theta_2 - \theta_0)\, e' \,(1 + f'\, \overline{\theta_2 + \theta_0})$$

where e' and f' are constants.

If at the junctions at temperature θ_0, the two circuits are joined in series, the electromotive force in the circuit is the difference of the above, and if we write it E_{210} we have

$$E_{210} = (\theta_2 - \theta_0)\, e' \,(1 + f'\, \overline{\theta_2 + \theta_0}) - (\theta_1 - \theta_0)\, e \,(1 + f\, \overline{\theta_1 + \theta_0}).$$

Let θ_2 become identical with θ_1, and let E_{110} now be the electromotive force in circuit. Then

$$E_{110} = (\theta_1 - \theta_0)\, e' \,(1 + f'.\overline{\theta_1 + \theta_0}) - (\theta_1 - \theta_0)\, e \,(1 + f\, \overline{\theta_1 + \theta_0}).$$

Therefore

$$E_{210} - E_{110} = (\theta_2 - \theta_1)\, e' \,(1 + f'\, \overline{\theta_2 + \theta_1}),$$

or

$$\theta_2 - \theta_1 = (E_{210} - E_{110})/e' \,(1 + f'\, \overline{\theta_2 + \theta_1}),$$

which furnishes a means of determining $\theta_2 - \theta_1$ from observations of the electromotive force when the circuits are in series, and of the electromotive force in the same circuits when the temperatures θ_2 and θ_1 are identical. In the tables which follow the quantity E_{210} is indicated by the term "Observed," and $E_{210} - E_{110}$ by the term "Reduced."

In the experiments, θ_0 is the temperature of the system of mercury cups (fig. 7, p. 401), indicated in what follows by J. The junctions in the discs are indicated by the letters U, M, C, B, for upper, middle, cover, and junction inside the air bath respectively.

Method of Experimenting.

In carrying out the test of a disc of any substance, the copper discs, between which the disc to be tested was to be placed, were first brought together, and the total thickness of the combination measured by means of a micrometer wire gauge. The thickness of the disc to be tested was then measured, the disc placed in the proper position between the copper discs, glycerine being used to improve the contacts, and the total thickness measured. The differences of the observed thicknesses is the thickness of the disc of the material used, plus that of the two layers of glycerine, and we know, therefore, the thickness of the glycerine layers, and can calculate their effect on the flow of heat.

The combination was then suspended in the centre of the air bath, with the plane surfaces of the discs vertical. An electric current was then sent through the heating coil of the discs, which increased in temperature and began to lose heat to the bath.

If the test was to be carried out at a moderate temperature, current was also sent through the coil encircling the air bath for a short time, then stopped. Owing to the heat supplied by the coil to the discs, and given up by them to the bath, the temperature of the bath remains higher than that of the air, and would eventually become constant. The currents through the coil of the discs, and through the coil round the bath, were, however, adjusted from time to time, in order to attain the steady state of temperature as quickly as possible. When the temperatures of the discs and of the air bath had remained constant for 10 or 15 minutes, observations of the wattmeter, and of the electromotive forces in the various thermo-circuits, were made, an interval of 5 or 10 minutes allowed to elapse, and the observations repeated. If the second set did not show that the steady state had been reached, the temperature of the bath was varied suitably, and observations repeated. In this way it was insured that the observations were made during a state which approximated with sufficient closeness (p. 404) to the steady state.

If the test was to be carried out at a lower temperature, cold water was allowed to circulate between the inner and outer walls of the air bath, the observations being taken as before.

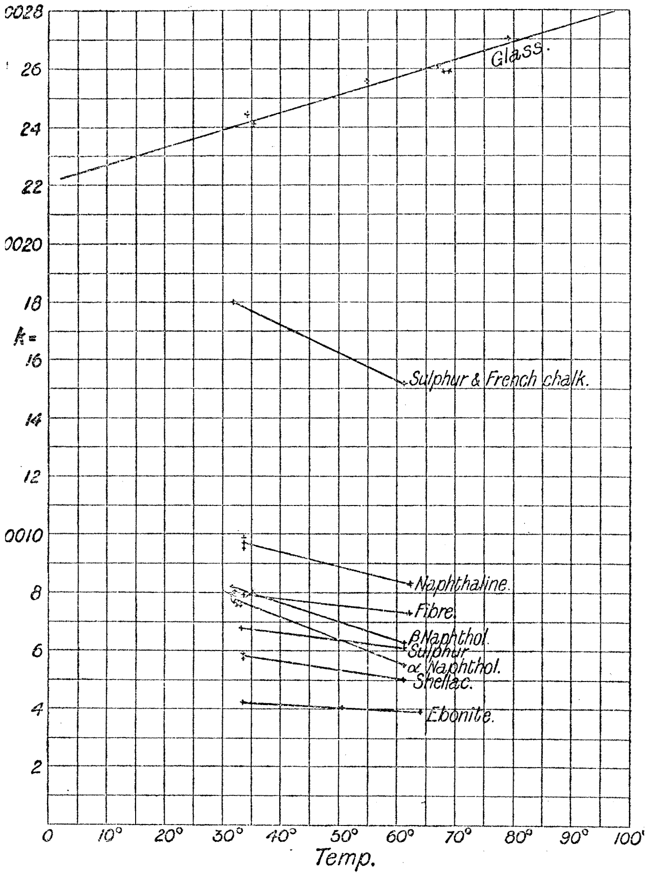
If the test was to be carried out at a higher temperature, the current through the heating coil was increased for a time, and current sent through the coil on the air bath till its temperature had been raised to the required amount. The current through the heating coil of the discs was then reduced to its normal amount, and the temperatures throughout allowed to become steady. Observations were taken as before. In cases where there was any suspicion of a change of the material under test having been brought about by the increase of temperature, for additional security the temperature of the bath was again lowered and a second test made at the original temperature.

The following tables and curves show the substances tested and the results obtained :

Substance.	t_S centims.	θ_J.	C ohms.	U ohms.	Divisor.	$\theta_C-\theta_J$.	θ_C.	$_U-\theta_J$.	θ_U.	U − M ohms.		Divisor.	$\theta_U-\theta_M$.	θ_M.	B ohms.	Divisor.	$\theta_B-\theta_J$.	θ_B.
										Observed.	Reduced.							
Glass (July 31)	·281	17°·92	6·44	6·21	·376	17°·13	35°·05	16°·52	34°·44	·400	·342	·383	°·893	33°·55	−0·64	·347	−1°·85	16°·07
		20·27	5·93	5·70	·377	15·73	36·00	15·12	35·39	·400	·348	·384	·905	34·48	−1·33	·348	−3·82	16·45
		20·51	19·00	18·75	·395	48·10	68·61	47·47	67·98	·520	·340	·419	·811	67·17	11·58	·367	31·55	52·06
Glass (Aug. 4)	·281	17·81	6·77	6·55	·376	18·01	35·82	17·42	35·23	·405	·345	·384	·898	34·33	−0·58	·346	−1·68	16·13
		18·43	14·52	14·30	·387	37·52	55·95	36·95	55·38	·487	·347	·406	·855	54·53	7·05	·357	19·75	38·18
		18·74	19·58	19·36	·394	49·70	68·44	49·14	67·88	·540	·350	·419	·835	67·05	11·84	·366	32·35	51·09
		19·05	24·60	24·32	·401	61·35	80·40	60·65	79·70	·590	·350	·434	·802	78·90	16·81	·373	45·07	64·12

	v_C.	v_U.	v_M.	Heat generated in gram degrees.	$(1·395+\frac{1}{4}t_S)\,v_M$.	$\frac{1}{4}t_S\,.\,v_U$.	Sum.	$(1·395+\frac{1}{2}t_S)\,v_M$.	$1·233\,.\,v_C$.	$(·442+\frac{1}{2}t_S)\,v_U$.	Sum.	Ratio of sums.	Heat transmitted.	Heat transmitted per sq. centim.	Temperature slope.	Conductivity.	Temperature.
Glass (July 31) (continued)	18°·98	18°·37	17°·48	·220	25·6	1·3	26·9	26·9	23·4	10·3	60·6	·444	·098	·00783	3°·18	·00246	34°
	19·55	18·94	18·03	·220	26·4	1·3	27·7	27·6	24·1	11·0	62·7	·442	·097	·00776	3·22	·00241	35
	16·55	15·92	15·11	·213	22·1	1·1	23·2	23·1	20·3	9·3	52·7	·440	·094	·00750	2·89	·00259	68
Glass (Aug. 4) (continued)	19·69	19·10	18·20	·220	26·7	1·3	28·0	28·0	24·4	11·1	63·5	·441	·0969	·00774	3·19	·00242	35
	17·77	17·20	16·35	·220	23·9	1·2	25·1	25·0	21·9	10·1	57·0	·440	·0971	·00776	3·04	·00256	55
	17·35	16·79	15·96	·220	23·4	1·2	24·6	24·6	21·4	9·9	55·9	·440	·0971	·00776	2·97	·00261	67
	16·28	15·58	14·78	·220	21·7	1·1	22·8	22·7	20·1	9·2	52·0	·438	·0962	·00770	2·85	·00270	79

Substance.	t_s centims.	θ_J.	C ohms.	U ohms.	θ_C.	θ_U.	U − M ohms.	$\theta_U - \theta_M$.	θ_M.	B ohms.	θ_B.	Heat generated.	$(1{\cdot}395 + \frac{1}{4}t_s)\, v_M + \frac{1}{4}t_s v_U$.	$(1{\cdot}395 + \frac{1}{2}t_s)\, v_M + 1{\cdot}233\, v_C + (\cdot442 + \frac{1}{2}t_s)\, v_U$.	Ratio of sums.	Heat transmitted.	Temperature slope.	Conductivity.	Temperature.
							Reduced.												
Naphthaline	·158	18·30	6·07	5·84	34·49	33·87	·440	1·15	32·72	−1·09	15·15	·209	26·0	60·8	·428	·0895	7·28	·000984	33
		18·51	17·41	17·18	63·13	62·55	·550	1·33	61·22	9·86	45·75	·209	22·9	54·3	·422	·0882	8·42	·000838	62
		18·57	6·01	5·78	34·60	33·98	·447	1·17	32·81	−1·20	15·09	·209	26·2	61·4	·427	·0892	7·41	·000964	33
		17·70	18·00	17·77	63·89	63·28	·550	1·33	61·95	10·52	46·68	·210	22·6	53·6	·422	·0886	8·42	·000842	62
		18·00	6·15	5·92	34·40	33·79	·457	1·20	32·59	−0·99	15·13	·209	25·9	60·6	·427	·0892	7·59	·000941	33
α Naphthol	·152	17·30	6·08	5·88	33·55	33·02	·500	1·31	31·71	−0·90	14·69	·205	25·1	59·5	·422	·0865	8·62	·000803	32
		17·53	17·58	17·38	62·61	62·09	·773	1·88	60·21	10·30	45·98	·206	21·0	51·2	·410	·0845	12·37	·000546	61
		17·52	6·17	5·97	33·97	33·44	·540	1·41	32·03	−0·91	14·88	·206	25·3	60·0	·422	·0869	9·28	·000749	33
β Naphthol	·166	17·07	6·13	5·91	33·46	32·87	·535	1·41	31·46	−0·75	14·90	·206	24·4	58·3	·419	·0863	8·49	·000813	32
		17·26	17·90	17·67	63·16	62·57	·750	1·82	60·75	10·56	46·43	·206	21·2	51·6	·411	·0847	11·0	·000616	61
		17·40	6·17	5·97	33·85	33·32	·540	1·41	31·91	−0·86	14·91	·206	25·1	60·7	·414	·0853	8·49	·000803	33
Sulphur	·193	16·86	6·48	6·28	34·19	33·65	·745	1·95	31·70	−0·62	15·06	·208	24·8	60·0	·413	·0859	10·1	·000680	33
		17·32	17·56	17·36	62·33	61·82	·89	2·17	59·65	10·20	45·58	·208	21·2	51·9	·409	·0851	11·2	·000608	61
		17·46	6·30	6·11	34·26	33·75	·74	1·94	31·81	−0·80	15·14	·207	25·0	60·2	·415	·0857	10·1	·000680	33
Sulphur and French chalk	·3195	17·54	5·90	5·70	33·32	32·78	·48	1·26	31·52	−0·86	15·05	·207	25·7	60·2	·427	·0884	3·95	·00179	32
		17·84	17·39	17·18	62·54	62·01	·60	1·46	60·55	10·31	46·32	·207	22·3	53·0	·421	·0871	4·58	·00152	61
		18·01	5·86	5·67	33·68	33·17	·48	1·26	31·91	−0·99	15·14	·207	26·2	61·4	·427	·0884	3·95	·00179	32
Ebonite	·130	17·72	6·32	6·11	34·53	33·97	·797	2·08	31·89	−0·81	15·38	·207	24·1	58·7	·411	·0851	16·0	·000426	33
		18·45	13·23	13·02	52·90	52·36	·85	2·11	50·25	6·08	35·53	·205	21·4	52·8	·405	·0830	16·2	·000410	51
		18·76	18·09	17·88	64·79	64·26	·89	2·15	62·11	10·83	48·51	·203	19·9	49·3	·404	·0820	16·5	·000398	63
		18·78	5·84	5·65	34·31	33·81	·77	2·02	31·79	−1·14	15·48	·198	23·8	57·8	·412	·0816	15·5	·000421	33
Shellac	·168 ·161	17·80	6·23	6·03	34·41	33·88	·76	1·99	31·89	−0·78	15·55	·207	24·1	58·7	·411	·0851	11·8	·000577	33
		18·43	17·48	17·27	63·14	62·60	·88	2·14	60·46	10·44	47·13	·208	19·7	49·1	·401	·0834	13·3	·000501	61
		18·60	6·02	5·82	34·61	34·08	·73	1·885	32·20	−1·00	15·71	·207	24·3	58·9	·413	·0855	11·7	·000585	33
Fibre	·121	18·00	5·94	5·74	33·84	33·31	·41	1·07	32·24	−0·96	15·22	·207	24·8	58·5	·424	·0878	8·85	·000793	33
		18·20	17·55	17·34	63·09	62·55	·47	1·14	61·41	10·29	46·55	·207	21·7	51·5	·421	·0871	9·42	·000740	62
		18·30	6·05	5·85	34·43	33·90	·41	1·07	32·83	−1·04	15·29	·207	25·5	60·0	·425	·0880	8·85	·000795	33



Remarks on preceding Tables.

In the first table the whole of the observations and reductions are shown, but in the second the observations and only the important steps in the reduction.

The thickness given in the tables is that of the material under test plus the two layers of glycerine. The correction for the glycerine is too small to be taken into account, except in the case of glass and of the mixture of sulphur and French chalk. The corrected values for glass are: at 35°, ·00248, ·00243, ·00244; at 55°, ·00258; at 68°, ·00261, ·00263; at 79°, ·00272, and for the cement at 32°, ·00182; at 61°, ·00155.

The glass was ordinary window glass, known as 22 oz. In the second series of experiments with it, the glycerine contact layers had been replaced by shellac (see p. 420).

The naphthaline disc was cast between glass plates and ground down to the required thickness.

The two naphthol discs were obtained by sawing slices from two large blocks of the material and grinding the surfaces.

The sulphur disc was made by pouring melted sulphur on to a glass plate and grinding the upper surface down till it was parallel to the lower, and the disc of the requisite thickness. The surface which had been in contact with the glass had a crystalline appearance, the other not.

The disc of sulphur and French chalk was made in the same way. It contained about equal quantities of the two constituents.

The shellac disc was cast between glass plates, and contained a few small air holes.

The fibre was the ordinary "white fibre" of electrical instrument makers.

As the result of these experiments, it may be stated that the tendency at about 40° C. of the thermal conductivities of solid substances not very good conductors of heat, is to diminish with increase of temperature, at a percentage rate which appears to vary with the nature of the substance. Amongst the materials tested, glass is the only exception to this rule.

Substance.	k_{35° C.	Mean percentage change per degree between 35° and 60° C.
Glass (22-oz. window)	·00245	+ ·0025
Naphthaline	·00095	— ·0052
α Naphthol	·00076	— ·0105
β "	·00080	— ·0085
Sulphur	·00067	— ·0036
Sulphur and French chalk	·00180	— ·0052
Ebonite	·00042	— ·0019
Shellac	·00058	— ·0055
White Fibre	·00079	— ·0020

The above values of the conductivities agree with those found by a different method (LEES, 'Phil. Trans.,' A, 1892, p. 506) for temperatures between 25° and 35°:—glass, ·00243; sulphur, ·00045; ebonite, ·00040; shellac, ·00060, except in the case of sulphur, where the large difference is probably due to the disc tested in the present experiment not being wholly crystalline.

PART II. CONDUCTIVITIES AND TEMPERATURE COEFFICIENTS OF LIQUIDS.

Preliminary Experiments.

The apparatus used originally in the experiments on the conductivities of liquids, consisted of two circular copper discs, *U* and *M*, cemented by rubber cement to the opposite sides of a circular sheet of rubber, *R*, fig. 10. To the free surface of the upper disc, a flat coil, *C*, of insulated platinoid wire was cemented, and served to supply the heat required in the experiment.

These discs were supported by means of a three-legged support, *T*, screwed to the upper disc, above the third copper disc, *L*, which was provided with a raised edge. The legs of the support were long enough to raise the lower surface of the disc, *M*, about ·13 centim. above the upper surface of the disc, *L*. The liquid, the thermal conductivity of which was to be determined, was poured on to the lower disc, where it was retained by the raised edge. The three discs were then placed on the horizontal top of a closed vessel through which a stream of cold water was kept flowing, and they could, if necessary, have a cover placed over them. On sending a current through the coil, *C*, part of the heat generated flowed through the discs to the top of the cold water vessel, the rest was lost by conduction and convection in the air above the coil. After the distribution of temperature has become steady, the heat flowing through the rubber from *U* to *M* proceeds either through the layer of liquid to *L*, or is lost from the surfaces of *M* and of the liquid. As the temperature of the water flowing through the vessel underneath the discs was always a few degrees less than that of the air of the room, it was possible, by regulating the rate of flow of the water, to arrange that the temperature of the surface from which this heat was lost was nearly identical with that of the air, and the loss was thus reduced to so small an amount that it could be neglected. By means of thermo-junctions of copper and platinoid wires, soldered into holes about 3 millims. deep in the edges the discs, *U* and *M*, and in holes 2 centims. deep in the edge of the disc, *L*, the temperature of the upper disc, and the differences of temperature between the upper and middle, and between the upper and lower discs, were found by balancing the thermo-electric E.M.F. in each case against the requisite fractional part of the E.M.F. of a Leclanché cell, which had been compared with a standard Clark cell. It was found that for small temperature differences the E.M.F.s so determined, could be taken as proportional to the differences of temperature.

Fig. 10.

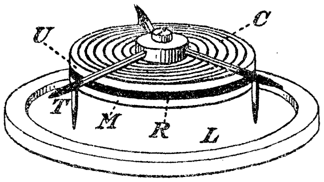


Fig. 11.

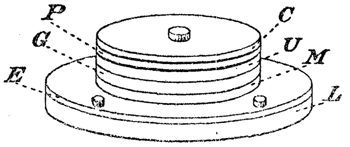
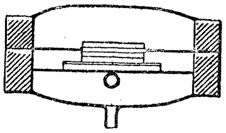


Fig. 12.



From the difference of temperature on the two sides of the rubber sheet, and the thickness area and conductivity of the rubber, the amount of heat entering the liquid could be calculated, and if the thickness of the liquid, the area of flow, and the difference of temperature are known, the thermal conductivity of the liquid can be found.

The curvature of the lines of flow in the liquid near the edge of the disc, *M*, will render the area of flow in the liquid greater than in the rubber, and a small correction would have to be applied if the thermal conductivity were made to depend on that of the rubber. It is better, however, to base the determination on the conductivity of water, which can be substituted for the liquid, and tested under the same conditions. In this case the areas of flow in the two liquids may be assumed to be equal, and the calculation simplified.

With the apparatus in this form, determinations of the thermal conductivities of water, ethyl alcohol, acetic acid, and glycerine were made.

The values found in different experiments for the relative conductivities of water and glycerine, and mixtures of them, were concordant, and are given in the following table along with H. F. WEBER'S[*] values for water and glycerine between 9° and 15°, but experiments on ethyl alcohol and acetic acid showed discrepancies which were, after some time, traced to the evaporation of the liquid at points not covered by the middle disc. As most of the liquids to be tested were more volatile than water and glycerine, it was decided to get rid of this evaporation by entirely enclosing the liquid, and the apparatus used throughout the greater part of the investigation was then constructed.

Liquid.	$U - M$.	$M - L$.	k.	Temp.	H. F. WEBER'S values.
	ohms.	ohms.			
Water	·97	·28	·00140[‡]	20° C.	·00136
[†]25 per cent. 20·8 " } glycerine in water	·93	·32	·00119	"	
50 " 44·2 " } " "	·953	·387	·00101	"	
75 " 70·4 " } " "	·91	·46	·00081	"	
Glycerine	·89	·52	·00070	"	·00067

Description of Apparatus.

Between two nickel-plated copper discs, U and M, fig. 11, p. 419, 4 centims. in diameter and ·3 centim. thick, a disc of glass, C, ·28 centim. thick, was cemented by means of thin layers of shellac. In order to prevent bubbles of air occurring in the layer of shellac, the surfaces of the copper and glass discs to be cemented together were each covered with a thin layer of shellac, which was allowed to dry. Both surfaces were then smeared with glycerine, and slid carefully together, air being prevented from getting between the surfaces by the presence of abundance of glycerine. Pressure and heat were then applied, the pressure forcing out the glycerine and bringing the layers of shellac into contact, and the heat joining them. Both contacts were made in this way, and withstood a large amount of usage without coming apart.

A flat spiral coil of platinoid wire, P, was placed on the top of the upper disc, U, and was held down by a thin copper disc, C, ·10 centim. thick, screwed to the disc, U. The coil was insulated from both discs by means of mica, and the surfaces of the discs exposed to the air were varnished to give them the same emissivity. This combination rested on the inner edge of a ring of ebonite, E, of 7 centims. external,

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[*] H. F. WEBER, 'Berliner Ber.,' 1885, p. 809.

[†] The upper numbers are percentages by weight; the lower percentages by volume.

[‡] Taken from the table, p. 425.

and 3·71 centims. internal diameter, which in turn was supported by a disc of nickel-plated copper, *L*, 7 centims. diameter and ·3 centim. thick, to which it was cemented by rubber cement.

The copper discs will be called in order downwards, the "cover," "upper," "middle," and "lower" copper discs, respectively.

The discs were placed with the flat surfaces horizontal,* in a flat cylindrical air bath, fig. 12, p. 419, consisting of an upper and a lower half, each capable of being heated by means of an insulated coil of platinoid wire wound round it, and the lower half provided with a compartment through which a stream of cold water could be sent to cool the bath rapidly. During a test of thermal conductivity, this compartment contained air only.

A thermo-junction was soldered inside the top of the upper part of the enclosure, and it is assumed that the air to which the top and side surfaces of the discs lose heat, has the temperature given by this thermo-junction. The thermo-junctions in the upper discs were those described (p. 419), and were arranged vertically under each other. In order to bring the junction in the lower disc vertically under those in the upper, the holes in the sides of the lower disc were made correspondingly deeper, and for a depth of 1·5 centims. wider than those in the upper discs, and were lined with thin glass tubes to prevent the wires making contact with the disc at any other points than the junctions.

The liquid to be tested was placed in the ebonite ring, and had therefore the same thickness as the ebonite.

The heat flowing through the under surface of the middle copper disc was conducted away partly by the liquid under test, partly by the ebonite. The amount conducted away by the ebonite could be calculated if the shape of the stream lines and the thermal conductivity of the ebonite were known. It is, however, much more accurate to determine this quantity by a separate experiment, substituting air for the liquid and so arranging the amount of heat supplied, that the temperature difference between the middle and lower discs is the same as in the experiment on the liquid. The heat conducted through the air is then small, and can be calculated from the known thermal conductivity of air.† The remainder of the heat flowing through the under surface of the middle disc is conducted through the ebonite to the lower disc, and is the quantity required.

Theory of Ebonite Ring Apparatus.

If r = radius of copper and glass discs,

t_G = thickness of glass disc,

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* The disc of liquid being thin, convection currents only come in to a slight extent when the discs are not quite horizontal. In the case of a disc of water, an inclination of 15° to the horizontal only increased the apparent conductivity 1 per cent.

† WINKELMANN'S value has been used, 'Wied. Ann.,' vol. 48, p. 186, 1895.

t_M = thickness of copper disc below glass, plus correction for thermo-wires,
r_l = radius of disc of liquid,
t_l = thickness of disc of liquid,
v_U = excess of temperature of upper disc over that of the air in the enclosure.
v_M = excess of temperature of middle disc ,, ,, ,,
v_L = excess of temperature of lower disc ,, ,, ,,

then the heat flowing through the glass disc per second

$$= \pi r^2 k_G \frac{v_U - v_M}{t_G},$$

the heat entering the middle disc

$$= \pi r^2 k_G \frac{v_U - v_M}{t_G} - 2\pi r h t_G \frac{v_U + v_M}{4},$$

and the heat leaving the middle disc by its under surface

$$= \pi r^2 k_G \frac{v_U - v_M}{t_G} - 2\pi r h \left(t_G \frac{v_U + v_M}{4} + t_M v_M\right).$$

The amount passing through the disc of liquid

$$= \pi r_l^2 k_l \frac{v_M - v_L}{t_l},$$

the amount entering the ebonite ring surrounding the liquid may be put*

$$= A \frac{v_M - v_L}{t_l},$$

where A is an unknown constant depending on the breadth of the ring under the middle copper disc, and on the distribution of the lines of flow in it. Between these quantities we have the relation†

$$(\pi r_l^2 k_l + A) \frac{v_M - v_L}{t_l} = \pi r^2 k_G \frac{v_U - v_M}{t_G} - 2\pi r h \left\{\frac{t_G}{4} \cdot v_U + \left(\frac{t_G}{4} + t_M\right) v_M\right\},$$

from which we can determine k_l if A, k_G and h are known, by observations of v_U, v_M, and v_L.

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* Strictly, a term Bv_L ought to be introduced here, since some of the lines of flow from the middle disc may pass through the ebonite to its upper surface. On account of the smallness of B, this term has been neglected.

† See note, p. (403).

The value of k_G and h are known from the observations made in Part I.

The value of A is determined most accurately, by carrying out an experiment with air substituted for the liquid, so that the term involving k_l on the left-hand side of the equation has a known small value. From the observations of temperature the value of the right-hand side of the equation is calculated, and hence the value of A.

Constants of Apparatus.

$r = 2$ centims., therefore $\pi r^2 = 12{\cdot}5$ sq. centims.
$r_l = 1{\cdot}855$ centims., therefore $\pi r_l^2 = 10{\cdot}8$ sq. centims.
$t_l = {\cdot}127$,,
$t_G = {\cdot}281$,, therefore $\frac{t_G}{4} = {\cdot}070$ centims.
$t_M = {\cdot}320 + {\cdot}075 = {\cdot}395$ centims.
$h = {\cdot}00030$, therefore $2\pi rh \frac{t_G}{4} = {\cdot}00026$
and $2\pi rh\, t_M = {\cdot}00148$
Sum $= {\cdot}00174$

Method of Experimenting with Ebonite Ring Apparatus.

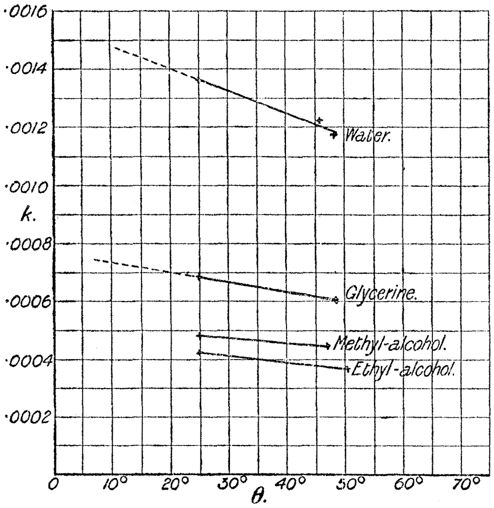
In carrying out a determination of the thermal conductivity of a liquid, the surfaces of the discs with which the liquid was to come into contact were cleaned, and the lower nickel-plated surface of the middle disc wet with the liquid. Liquid was then poured into the space inside the ebonite ring, till the upper surface of the liquid was higher than the upper surface of the ring. The middle disc was then placed on the ebonite ring with one edge touching the liquid, which was drawn into the space between disc and ring by capillarity. The disc was then slid slowly over the ring till the liquid was entirely enclosed, and any excess which flowed over the ring was removed by filter paper.

To prevent the upper discs moving during an experiment, they were secured to the lower, either by a silk thread passing from one side of the lower disc over the upper discs to the other side of the lower disc, or by a wire frame which could be attached to the lower disc, and was provided with a screw which pressed on a small disc of cork on the copper disc covering the heating coil.

The combination was then placed in the air bath and the process described (p. 413) carried out till the steady temperature state was attained, when the observations of power supplied, temperatures, and temperature differences were made.

Experiments were made on four liquids, with the results given in the following tables and curves.

Liquid.	θ_J.	U.	θ_U.	Reduced.		$\theta_M-\theta_L=v_M-v_L$.	θ_M.	B	θ_B.	Temperature slope in glass.	Heat transmitted through glass.	·00026 v_U.	·0017 v_M.	Heat transmitted through liquid and ebonite.	Temperature slope in liquid.	Heat transmitted per unit slope through liquid and ebonite.	Heat transmitted through liquid.	Heat transmitted per square centim. $= k$.	Temperature.
				U − M.	M − L.														
	°	ohms.	°	ohms.	ohms.	°	°	ohms.	°										°
Water	16·74	3·48	26·14	·600	0·480	1·28	24·54	1·3	20·29	5·69	·168	·002	·007	·159	10·1	·0157	·0148	·00137	24
	16·91	12·02	48·38	·580	0·560	1·41	46·93	10·32	44·01	5·18	·162	·001	·005	·156	11·1	·0141	·0132	·00122	46
	17·26	3·61	26·96	·590	0·475	1·27	25·39	1·28	20·76	5·59	·166	·002	·008	·156	10·0	·0156	·0147	·00136	25
	16·80	12·68	49·91	·563	0·570	1·43	48·50	11·16	46·09	5·01	·157	·000	·004	·153	11·3	·0135	·0126	·00117	48
Air	17·42	4·22	28·80	·340	2·56	6·86	26·89	1·05	20·17	3·24	·096	·002	·012	·082	54·0	·0152	·0064	·000059	23
Glycerine . .	17·27	4·04	28·17	·590	0·890	2·37	26·60	1·77	22·08	5·59	·166	·002	·008	·156	18·9	·0825	·0737	·000682	25
	17·50	12·62	50·45	·550	0·970	2·44	49·08	10·55	45·20	4·87	·153	·002	·007	·144	19·2	·0750	·0662	·000613	48
Ethyl alcohol .	17·95	3·79	28·16	·570	1·28	3·40	26·65	0·99	20·65	5·37	·159	·002	·010	·147	26·8	·0548	·0460	·000426	25
	17·38	14·09	53·98	·530	1·44	3·58	52·67	11·77	48·19	4·66	·147	·002	·008	·137	28·2	·0486	·0398	·000369	51
Methyl alcohol .	18·30	12·13	49·97	·520	1·21	3·04	48·67	9·95	44·42	4·63	·145	·002	·007	·136	23·9	·0569	·0498	·000445	47
	18·21	3·84	28·56	·575	1·16	3·08	27·04	1·11	21·23	5·40	·160	·002	·010	·148	24·2	·0612	·0524	·000485	25



Liquid.	k_{25}.	Mean percentage change per degree between 25° and 45°.	$k_{9-15^{\circ}}$, H. F. W.
Water	·00136	—·0055	·00136
Glycerine	·00068	—·0044	·00067
Methyl alcohol	·00048	—·0031	·000495
Ethyl alcohol	·00043	—·0058	·000423

On account of the rapid way in which the methyl alcohol evaporated, it was necessary to work quickly, and the numbers given for it are not quite as reliable as those given for the other liquids.

The last column contains the values obtained by H. F. WEBER,* for the mean thermal conductivities between 9° and 15°.

As a result of the experiments, we may state that the thermal conductivities of liquids decrease with increase of temperature in the neighbourhood of 30° C., at a percentage rate which appears to be roughly the same for a number of liquids.

PART III. CHANGE OF CONDUCTIVITY ON MELTING.

Combining the last result with the one obtained for solids, Part I., and with the fact that solids in general conduct heat better than liquids, and liquids better than gases, we are led to conjecture that a given substance will, as its temperature is increased, decrease in conductivity, and that the decrease will continue during any change of state which the substance may undergo, owing to the increase in temperature. The

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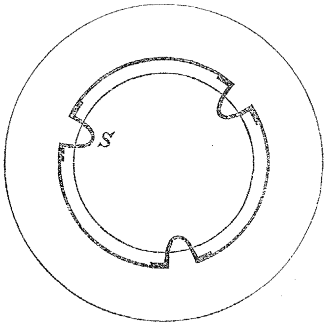
* H. F. WEBER, 'Berliner Ber.,' 1885, p. 809.

question then arises: Is there any sudden change in the conductivity as the substance passes from one physical state to another, or is this change continuous?

In order to test what change occurs in the thermal conductivity of a substance as it passes from the solid to the liquid state, the apparatus used for liquids was modified slightly, so as to allow space between the lower and middle discs for change of volume of the substance tested on melting.

The ebonite ring was replaced by one of "white fibre," pierced by a hole 4·16 centims. in diameter, *i.e.*, greater in diameter than the middle copper disc (fig. 13), with three strips, *S*, of fibre projecting inwards, in order to provide support for the middle disc, and keep the layer of substance tested of constant thickness. By means of a wire frame attached to the lower disc, and a screw, the upper discs were pressed down on to the strips of fibre, and the lifting of the upper discs, owing to expansion of the substance tested on melting, prevented.

Fig. 13.



Some of the substance to be heated was placed within the ring, and the lower disc heated till the substance melted. The upper discs were then placed in position and the apparatus allowed to cool. The experiment was then conducted as in a test of a liquid.

The area of the projecting lugs of the fibre disc, through which heat could flow, was estimated as approximately ·4 centim., hence the heat transmitted per second per unit slope of temperature through the fibre, and not through the substance under test, would be = ·0003 gram degrees approximately.* The nett area of flow through the substance has been taken = 13·3 sq. centims., but as this number is, to some extent, uncertain, owing to the difficulty of obtaining discs which, in the solid state, completely filled the space within the fibre ring, the results given in the following table for different substances are not comparable with each other to within 3 or 4 per cent., although those for the same substance, at different temperatures, are.

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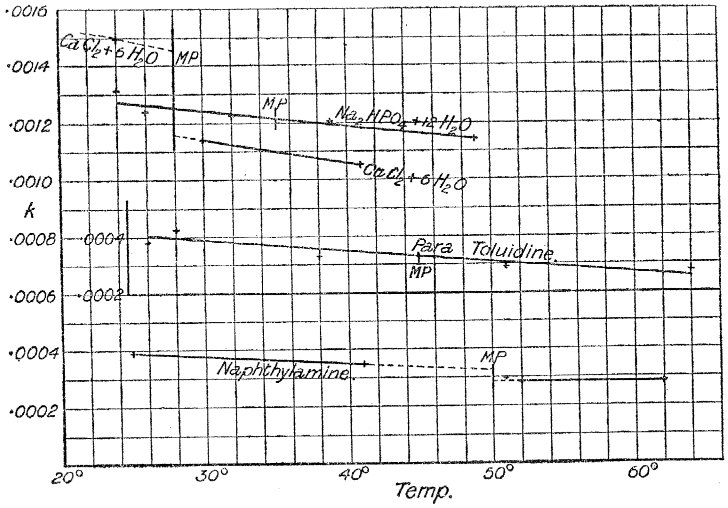
* The conductivity of the fibre = ·0008 (pp. 417, 418).

Substance.	Thickness, centims.	θ_J.	U.	θ_U.	Ohms reduced.		$\theta_M-\theta_L$.	θ_M.	B.	θ_B.	Temperature slope in glass.	Heat transmitted through glass.	·00026 v_U.	·0017 v_M.	Heat transmitted through substance and fibre.	Temperature slope in substance.	Total heat/slope.	Heat through substance/slope.	Conductivity.	Temperature.
					U−M.	M−L.														
		°	ohms.	°			°	°	ohms.	°										°
$Na_2HPO_4+12H_2O$	·125	15·82	3·72	25·92	·61	0·425	1·14	24·29	1·30	19·37	5·81	·171	·002	·008	·161	9·12	·0177	·0174	·00131	24
m.p. = 35° C.		16·26	6·76	34·29	·597	0·453	1·19	32·73	4·52	28·44	5·55	·167	·002	·007	·158	9·52	·0166	·0163	·00123	32
		16·68	9·16	40·91	·586	0·47	1·21	39·40	7·17	35·75	5·375	·165	·002	·006	·157	9·62	·0163	·0160	·00120	39
		16·87	12·91	50·58	·585	0·505	1·27	49·12	11·45	46·92	5·20	·163	·001	·004	·158	10·2	·0155	·0152	·00114	49
		16·67	4·33	28·34	·615	0·455	1·21	26·71	1·98	22·06	5·80	·173	·002	·008	·163	9·68	·0168	·0165	·00124	26
$CaCl_2+6H_2O$ . .	·125	16·46	3·60	26·24	·63	0·385	1·03	24·54	1·24	19·9	5·98	·177	·002	·008	·167	8·24	·0203	·0200	·00150	24
m.p. = 29° C.		16·81	5·79	32·29	·62	0·50	1·32	30·66	3·4	26·00	5·80	·174	·002	·008	·164	10·6	·0155	·0152	·00114	30
		17·15	9·71	42·75	·60	0·535	1·37	41·22	7·3	36·5	5·44	·168	·002	·008	·158	11·0	·0144	·0141	·00106	41
Air	..	18·20	2·59	25·22	·19	1·85	4·99	24·71	0·58	19·78	1·81	·053	·002	·008	·043	39·9	·0011	·00078	·000059	22
Naphthylamine .	·107	17·82	3·81	28·09	·58	1·10	2·93	26·55	1·08	20·76	5·48	·162	·002	·010	·150	27·4	·00547	·0052	·00039	25
m.p. = 50° C.		18·16	9·75	43·82	·565	1·27	3·25	42·38	7·37	37·73	5·12	·158	·002	·008	·148	30·4	·00487	·0046	·00035	41
		18·24	13·60	53·56	·533	1·467	3·66	52·24	11·15	47·51	4·70	·148	·002	·008	·138	34·2	·00404	·0037	·00028	52
		18·50	18·20	64·93	·520	1·495	3·63	63·67	15·76	59·12	4·48	·145	·002	·008	·135	33·9	·00398	·0037	·00028	62
Para-Toluidine .	·107	17·82	4·04	28·68	·555	1·065	2·84	27·21	1·15	21·13	5·23	·155	·002	·010	·143	26·5	·00540	·0051	·00038	26
m.p. = 45° C.		18·55	8·34	40·55	·563	1·204	3·103	39·10	(6·8)	29·35	5·16	·158	·003	·017	·138	29·0	·00473	·0044	·00033	38
		18·85	13·32	53·56	·52	1·355	3·38	52·27	10·81	47·22	4·59	·145	·002	·009	·134	31·6	·00424	·0039	·00029	51
		18·76	19·30	67·74	·50	1·455	3·48	66·55	16·89	61·96	4·23	·138	·002	·008	·128	32·5	·00394	·0036	·00027	64
		18·50	4·80	31·37	·65	1·22	3·23	29·65	3·95	29·12	6·11	·183	·001	·001	·181	30·2	·00600	·0057	·00043	28



The experiments show no apparent break in the regularity of the change of thermal conductivity at the melting point in the case of three of the solids, and a decrease of about 20 per cent. in the case of $CaCl_2 + 6H_2O$.*

This salt was extremely difficult to work with, on account of the rate at which it absorbed moisture, and the results obtained cannot be relied on to the same extent as those for the other substances.

It seems, then, reasonable to conclude that, for salts at least, change of state on melting is not invariably accompanied by an abrupt change of thermal conductivity.

PART IV. THERMAL CONDUCTIVITIES OF MIXTURES.

After coming to the above conclusions with respect to pure, or approximately pure, substances, one is led naturally to experiment on mixtures of substances, and, since mixtures of liquids are most easily made, they were the first on which observations were carried out.

It is obviously advantageous to investigate mixtures of pairs of liquids, the conductivities of which differ as widely as possible. The number of miscible liquids which satisfy this condition is small, owing to the great number of organic liquids which have conductivities nearly alike. Water and glycerine are much better conductors than most liquids, and have, therefore, been used in several mixtures.

The following mixtures of water, ethyl alcohol, methyl alcohol, acetic acid, glycerine, and sugar were made, and their thermal conductivities investigated :—

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* BARUS ('Sill. Journal' (3), vol. 44, p. 1, 1892), has found a decrease of about 15 per cent. in the case of thymol, which melts at about 12·5° C.

Glycerine in water	25, 50, 75 per cent., by weight. 20·8, 44·2, 70·4 per cent., by volume.
Ethyl alcohol in water*	25, 50, 75 per cent., by weight. 30, 58, 81 per cent., by volume.
Methyl alcohol in water	23·9, 50, 74·7 per cent., by weight. 28·8, 58, 80·7 per cent., by volume.
Acetic acid in water	25, 50, 75 per cent., by weight. 24, 48·7, 74 per cent., by volume.
Glycerine in ethyl alcohol . . .	25, 49·2, 74·8 per cent., by weight. 17·4, 38·7, 65·3 per cent., by volume.
Methyl alcohol in ethyl alcohol .	25, 48·5, 74 per cent., by weight and by volume.
Sugar in water	25, 50, 67 per cent., by weight. 17·2, 38·8, 62·6 per cent., by volume.

Some of the experiments were carried out with the ebonite ring apparatus, fig. 11, p. 419, some with the earlier form of apparatus, fig. 10.

The following table gives the experiments made with the former apparatus :—

Constants of Apparatus.

$r = 2$ centims. $\pi r^2 = 12{\cdot}5$ sq. centims.
$r_l = 1{\cdot}855$,, $\pi r_l^2 = 10{\cdot}8$,,
$t_l = 0{\cdot}127$,,
$t_G = 0{\cdot}281$,, $\dfrac{t_G}{4} = {\cdot}070$ centims.
$t_M = {\cdot}320 + {\cdot}075 = {\cdot}395$ centims.
$h = {\cdot}00030,$ $2\pi rh\dfrac{t_G}{4} = {\cdot}00026$
$2\pi rh\, t_M = {\cdot}00148$
Sum $= {\cdot}00174$

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* Henneberg, 'Wied. Ann.,' vol. 36, p. 146, 1889, obtained results for mixtures of water and ethyl alcohol which agree closely with those that follow.

Liquid.	θ_J.	U.	θ_U.	Reduced.		$\theta_M - \theta_L$.	θ_M.	B.	θ_B.	Temperature slope in glass.	Heat transmitted through glass.	$\cdot 00026 v_M$.	$\cdot 0017_M$.	Heat transmitted through liquid and ebonite.	Temperature slope.	Total heat/slope.	Heat through liquid/slope.	Conductivity.	Temperature.
				U − M.	M − L.														
	°	ohms.	°	ohms.	ohms.	°	°	ohms.	°										°
Water	12·84	·57	14·4	·687	0·528	1·46	12·5	+·02	13·0	6·76	·194	·0004	−·0009	·194	11·5	·0169	·0160	·00149	11
25 %* 30 Ethyl alcohol in H_2O	13·22	·07	13·4	·715	0·735	2·14	11·4	−·24	12·5	7·05	·202	·0003	−·0019	·204	16·8	·0121	·0112	·00104	10
50 % 58 do.	13·76	·23	14·4	·702	0·957	2·65	12·5	−·22	13·2	6·91	·198	·0004	−·0012	·199	20·9	·0095	·0086	·00079	11
75 % 81 do.	13·96	·48	15·3	·681	1·202	3·33	13·4	−·21	13·4	6·73	·193	·0006	·0000	·192	26·2	·0073	·0064	·00059	12
Ethyl alcohol	13·84	·22	14·4	·692	1·492	4·13	12·5	−·32	12·9	6·83	·196	·0004	·0007	·196	32·5	·0060	·0051	·00047	10
25 % 24 Acetic acid in H_2O	13·92	−·23	13·3	·715	0·691	1·91	11·3	−·33	12·9	7·05	·202	·0001	·0027	·205	15·0	·0136	·0127	·00118	11
50 % 48·7 do.	14·12	−·09	13·9	·704	0·879	2·44	12·0	−·32	13·2	6·94	·199	·0002	·0020	·201	19·2	·0105	·0096	·00088	11
75 % 74 do.	12·86	+·76	15·0	·680	1·110	3·08	13·1	−·04	12·8	6·69	·191	·0007	·0005	·191	24·2	·0079	·0070	·00064	11
Acetic acid	13·28	+·64	15·1	·670	1·551	4·30	13·2	−·20	12·7	6·62	·190	·0007	·0009	·190	33·9	·0056	·0047	·00043	11
25 % ethyl alcohol in H_2O	13·80	−·36	12·8	·715	0·753	2·09	10·8	−·34	12·8	7·05	·202	.0000	·0034	·205	16·4	·0125	·0116	·00107	9

* The upper numbers are per cents. by weight, the lower by volume.

The conductivities given in the preceding table depend on that of the disc of glass between the upper and middle copper discs, which was determined in Part I.

Previous to the apparatus with the glass disc being constructed, experiments had been carried out with the apparatus in which rubber replaced the glass. As the conductivity of this rubber was unknown, the results obtained were all expressed in terms of the conductivity of water. By means of the value for water found in Part II., these relative values have been converted into absolute values, and are given in the table which follows.

The discs were not in this case surrounded by a vessel of known temperature, but were exposed to the air, the temperature of which was observed. The lower disc was placed in the top of a vessel through which cold water circulated, and the observations were taken in the manner previously described.

The theory of the method is identical with that given on p. 422, except that the constant A is zero.

Constants of Apparatus.

$r = 2$ centims. $\pi r^2 = 12{\cdot}5$ sq. centims.

$r_l = 1{\cdot}855$,, $\pi r_l^2 = 10{\cdot}8$,,

$t_l = {\cdot}132.$

$t_R = {\cdot}110$, therefore $t_R/4 = {\cdot}027$ centims.

$t_M = {\cdot}320 + {\cdot}075 = {\cdot}395$,,

$h = {\cdot}00030$, therefore $2\pi rh\, t_R/4 = {\cdot}00010$

$2\pi rh\, t_M = {\cdot}00148$

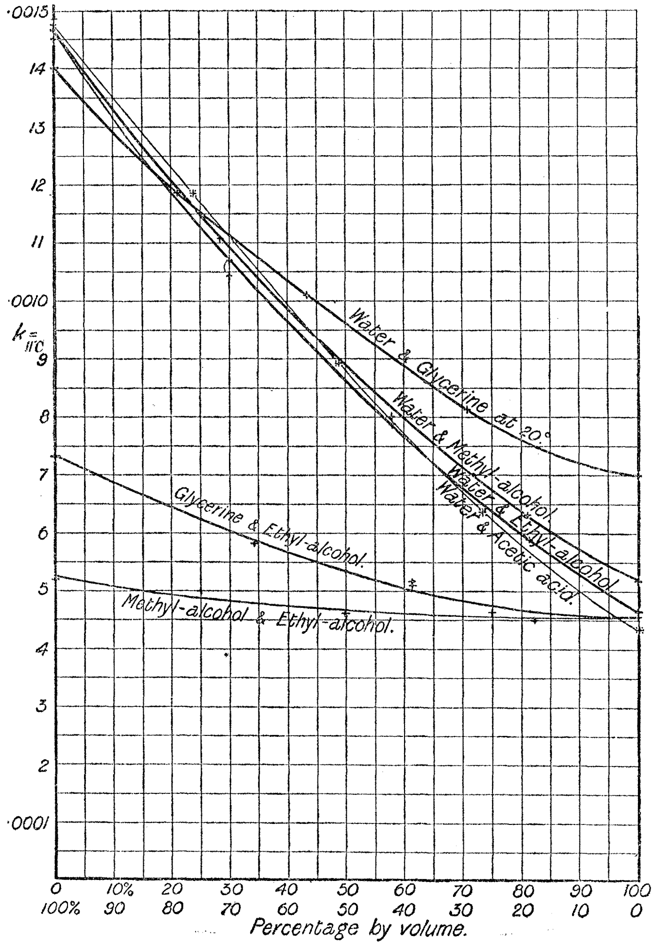
Sum . . $= {\cdot}0016$

	θ_J.	U.	U − M.	M − L.	v_U.	$v_U - v_M$.	$v_M - v_L$.	v_M.	Heat through rubber.	$\cdot 0001 v_U$.	$\cdot 0016 v_M$.	Heat transmitted through liquid and ebonite.	Temperature slope in liquid.	Heat through liquid per unit slope.	Conductivity.	Temperature of liquid.	k_{11° C.
	°	ohms.	ohms.	ohms.	°	°	°	°								°	
Water	20	0·70	1·17	·31	1·9	3·17	0·84	−1·3	·101	·0002	−·002	·103	6·37	·0152	·00141†	18	·00147
„	20	0·70	1·215	·325	1·9	3·29	0·88	−1·4	·105	·0002	−·002	·107	6·67	·0151	·00139	18	·00145
Ethyl alcohol	20·5	1·00	1·19	·89	2·7	3·23	2·41	−0·5	·103	·0003	−·001	·104	18·3	·0048	·00044	19	·00046
„ {25 * / 17·4*} per cent. glycerine	20 20	1·26 1·13	1·17 1·153	·89 ·877	3·4 3·1	3·17 3·12	2·41 2·38	+0·2 0·0	·101 ·099	·0003 ·0003	·000 ·000	·101 ·099	18·3 18·0	·0046 ·0046	·00043 ·00043	19 19	·00045 ·00045
„ {50 / 38·7} „ „	20	1·0	1·165	·795	2·7	3·16	2·15	−0·5	·101	·0003	−·001	·102	16·3	·0054	·00050	19	·00052
„ {75 / 65·3} „ „	21	0·90	1·175	·718	2·4	3·18	1·95	−0·8	·101	·0002	−·001	·102	14·8	00·60	·00056	19	·00058
Glycerine	..	..	..	..	..	..	..	..	..	..	..	..	..	..	·00070‡	19	..
Water	20·1	0·73	1·18	·315	2·0	3·20	0·854	−1·2	·102	·0002	−·002	·104	6·47	·0152	·00141	19	·00148
„ {25 / 28·8} per cent. methyl alcohol .	20·6	0·61	1·183	·404	1·7	3·21	1·095	−1·5	·102	·0002	−·002	·104	8·30	·0116	·00107	19	·00111
„ {50 / 58} „ „	20·7	0·69	1·12	·52	1·9	3·04	1·41	−1·1	·097	·0002	−·002	·099	10·7	·0084	·00078	19	·00080
„ {75 / 80·7} „ „	21	0·69	1·10	·63	1·9	2·98	1·71	−1·1	·095	·0002	−·002	·097	13·0	·0066	·00061	19	·00063
Methyl alcohol	20·9	0·77	1·13	·77	2·1	3·06	2·09	−1·0	·098	·0002	−·002	·100	15·8	·0054	·00050	19	·00052
„ 25 per cent. ethyl alcohol .	20·9	0·90	1·17	·82	2·4	3·17	2·22	−0·8	·101	·0002	−·001	·102	16·8	·0052	·00048	20	·00050
„ 50 „ „ .	18·3	1·46	1·08	·76	4·0	2·93	2·06	+1·1	·093	·0004	+·002	·091	15·6	·0049	·00045	18	·00046
„ 75 „ „ .	18·5	1·54	1·095	·815	4·2	2·97	2·21	+1·2	·095	·0004	+·002	·093	16·7	·0047	·00044	18	·00046
Water {25 / 17·2} per cent. sugar	18	0·82	1·15	·35	2·2	3·12	0·95	−0·9	·100	·0002	−·001	·101	7·2	·0131	·00122	17	
„ {52 / 38·8} „ „	19	0·9	1·14	·41	2·4	3·09	1·11	−0·7	·099	·0002	−·001	·100	8·4	·0110	·00102	17	
„ {67 / 62·6} „ „	19	0·92	1·16	·48	2·5	3·14	1·30	−0·6	·100	·0003	−·001	·101	9·85	·0094	·00087	18	
Ammonia $\rho = \cdot 907 =$ {26 / 36} per cent. of liquid ammonia	19	1·00	1·14	·385	2·7	3·09	1·04	−0·4	·099	·0003	−·001	·100	7·9	·0118	·00109	18	

* Upper numbers by weight, lower by volume, throughout.

† Taken from table, p. 424.

‡ Taken from table, p. 420.



When the results given in these two tables are expressed by curves, with composition by weight as abscissæ and conductivities as ordinates, the curves for mixtures of methyl and ethyl alcohol and glycerine with water differ widely from each other, and no general law connecting the conductivities of mixtures directly with the conductivities and relative masses of the constituents can be traced. If, however, proportions by volume are taken as abscissæ, instead of proportions by weight, the curves for mixtures of methyl and ethyl alcohol and acetic acid with water become nearly identical, and we are led to the conclusion that in further work proportion by volume should be made the basis of comparison.

A further conclusion from an inspection of these curves is that the conductivity of a mixture of two liquids is less than the value calculated by the linear formula

$$k = \frac{k_1 v_1 + k_2 v_2}{v_1 + v_2},$$

when k_1 and k_2 are the conductivities, v_1 and v_2 the volumes, of the constituents present, and that the difference is greater the greater the difference in the conductivities of the constituents.

It is evident, therefore, that to investigate the law of variation of conductivity of a mixture with its constitution more closely, it is advisable to work with mixtures of constituents which differ in conductivity to a greater extent. If we confine ourselves to liquids, we are limited to ratios of conductivities of about one to three, and we must turn to mixtures of solids, or of solids and liquids to get greater ratios. In the case of mixture of solids with liquids which dissolve them, a difficulty arises as to which conductivity of the material entering into solution ought to be used in making the comparison—that of the material when in the solid, or when in the liquid state.

[The results given in the previous table for solutions of sugar in water are almost identical with those of mixtures of glycerine and water, so that it may be said that a solution of sugar behaves as if it were a mixture of water and a liquid having the same density as sugar and a thermal conductivity of ·0007. I have, however, found, by the method described by me in 'Manchester Memoirs,' vol. 42, No. 5 (1898), that the thermal conductivity of the solid sugar was about ·0012, so that from a knowledge of the thermal conductivity of a solid we can infer little or nothing as to how it will behave when it enters into solution. Thus, JÄGER, 'Wien. Ber.,' vol. 99, p. 245 (1890), found that solutions of sodium chloride, potassium chloride, and zinc sulphate of about the same strengths had conductivities nearly alike and slightly less than that of water, whereas I have found ('Manchester Memoirs' as above) that the first two salts in the solid state conduct eight or nine times as well as water, and the latter a little better than water. The result for ammonia solution given in the above table points in the same direction, so that it seems advisable, for the present at least, to confine our attention to mixtures in which neither constituent has changed its physical state. The further question, whether such mixtures should be treated as physical mixtures or as chemical compounds, must be held over till more information has accumulated.—13th June, 1898.]

If, on the other hand, solids are mixed with liquids in which they are not soluble, there is great difficulty in keeping the mixture experimented on uniform, and in determining its exact constitution.

These considerations point to the conclusion that mixtures of solids would be most useful in leading to the discovery of any law. They have, however, the disadvantage of not being as readily made as mixtures of liquids, a disadvantage which may be removed by using as one constituent a semi-solid like lard or vaseline.

A series of experiments have, therefore, been made with the apparatus, fig. 11, p. 419, on mixtures of one of these substances with various amounts of reduced iron, marble, zinc sulphate, and sugar, in the form of powder, and the results are given in the following table and curves :—

Materials, per cent. by volume.	θ_J.	U.	U−M.	M−L.	v_U.	v_U-v_M.	v_M-v_L.	v_M.	Heat transmitted through glass.	·00026 v_U.	·0017 v_M.	Heat transmitted through mixture and ebonite.	Temperature slope.	Heat transmitted per unit slope.	Heat per unit slope through liquid.	k.
Lard	16°·7	·73	·671	1·456	2°·0	1°·85	4°·03	+0°·2	·192	·0006	·0003	·191	31·7	·00602	·0051	·00047
,, ...	14·8	·92	·669	1·413	2·5	1·85	3·90	0·7	·192	·0008	·0012	·190	30·7	·00618	·0053	·00049
,, +10·8 per cent. reduced iron	..	·61	·674	1·130	1·7	1·86	3·12	−0·2	·193	·0005	−·0003	·193	24·6	·00784	·0069	·00064
,, +19·4 ,, ,,	..	·37	·693	0·851	1·0	1·91	2·36	−0·9	·198	·0003	−·0015	·199	18·6	·0106	·0097	·00090
,, +32·3 ,, ,,	..	−·18	·717	0·600	−0·5	1·98	1·66	−2·5	·206	−·0002	−·004	·210	13·1	·0160	·0151	·00140
,, +23·8 per cent. $ZnSO_4$	..	+·65	·661	1·193	+1·8	1·83	3·29	0·0	·189	·0005	·0000	·189	25·9	·00730	·0064	·00059
,, +37·5 ,, ,,	..	·43	·691	1·036	1·2	1·91	2·86	−0·7	·198	·0004	−·0012	·199	22·5	·00883	·0080	·00074
,, +55·5 ,, ,,	..	·79	·681	0·890	2·2	1·88	2·46	+0·3	·195	·0007	·0005	·194	19·4	·0105	·0091	·00084
,, +13·0 per cent. sugar	..	·50	·693	1·407	1·4	1·91	3·89	−0·5	·198	·0004	−·0008	·198	30·6	·00647	·0056	·00052
,, +38·0 ,, ,,	..	·70	·691	1·224	1·9	1·91	3·38	0·0	·198	·0006	·0000	·197	26·6	·00739	·0065	·00058
Lard	..	·61	·663	1·446	1·7	1·83	4·00	−0·1	·199	·0005	−·0002	·189	31·5	·00600	·0051	·00047
Vaseline	..	·88	·690	1·617	2·4	1·91	4·46	+0·5	·198	·0007	+·0008	·196	35·1	·00558	·0047	·00044
,, +25 per cent. marble	..	·70	·691	1·172	1·9	1·91	3·24	0·0	·198	·0006	·0000	·197	25·5	·00771	·0068	·00063
,, +43 ,, ,,	..	−·22	·731	0·779	−0·6	2·02	2·15	−2·6	·209	−·0002	−·0044	·213	16·9	·0126	·0117	·00108
,, +60 ,, ,,	..	−·28	·727	0·483	−0·8	2·01	1·33	−2·8	·208	−·0002	−·0048	·213	10·5	·0202	·0193	·00179
Marble	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	·0071*

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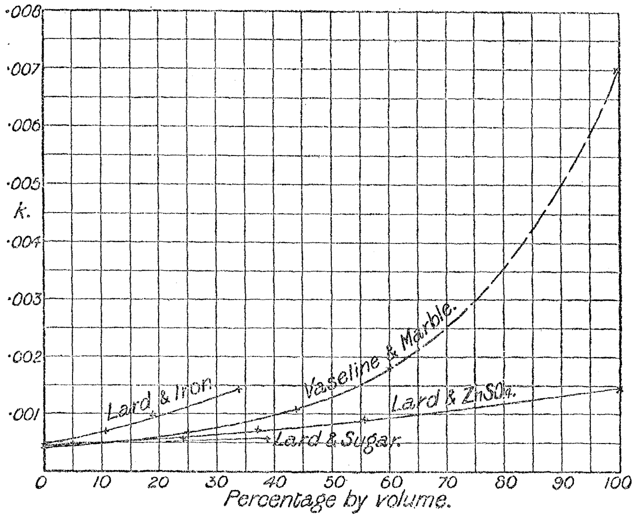
* From LEES, 'Phil. Trans. Roy. Soc.,' A, vol. 90, p. 506 (1892).



These results, taken in conjunction with those found for liquids and solutions, show conclusively that the thermal conductivity of a mixture is not a linear function of its composition. The observed conductivity is always less than that calculated from the linear law, and, on the other hand, greater than that calculated on the assumption that the resistivity is a linear function of the composition. The second assumption is, however, a closer approximation to the observed facts than the former.

Since neither of these simple assumptions seems capable of representing the facts, which, by their uniformity, appear, notwithstanding, to point to some general law of mixtures, it seemed advisable to calculate the conductivity of a model of a mixture built up in some simple way so as to lend itself readily to the process.

Suppose a cubic centimetre of some substance, having a conductivity ρ_0, to be divided by equidistant planes parallel to its faces, into 1000 small cubes of 1 millim. edge; and let n small cubes of the same size but of a material of conductivity ρ be substituted for n of the cubes of the cubic centimetre chosen at random. The large cube is then a mixture of two materials, and its conductivity may be readily calculated if the lines of flow are assumed to be parallel to one edge of the cube.

If ρ_0 is the thermal resistivity of the original, ρ that of substituted small cubes, the probability that, when n are substituted, p of them will be found in any column chosen at random,

$$= \frac{n!\,(1000-n)!}{p!\,(n-p)!\,(10-p)!\,(1000-n-10-p)!} \Big/ \frac{1000!}{10!\,990!}$$

$$= \frac{n!\,(1000-n)!\,10!\,990!}{p!\,(n-p)!\,(10-p)!\,(990-n+p)!\,1000!}$$

and the heat conducted through such a column, when its ends differ in temperature 1° C.,

$$= \frac{n!\,(1000-n)!\,10!\,990!}{p!\,(n-p)!\,(10-p)!\,(990-n+p)!\,1000!} \cdot \frac{10}{(10-p)\,\rho_0 + p\rho}.$$

Hence the conductivity of the mixture on the assumption that cross-transmission from column to column may be neglected,

$$= \sum_{p=0}^{p=10} \frac{n!\,(1000-n)!\,10!\,990!}{p!\,(n-p)!\,(10p)!\,(990-n+p)!\,1000!} \cdot \frac{10}{(10-p)\,\rho_0 + p\rho}.$$

The values of the factorial expressions have been calculated for $n = 200$, 400, 600, and 800 with the aid of De Morgan's tables of $n\,!$* and are as follows :—

p.	$n = 200$	$n = 400$	$n = 600$	$n = 800$
0	·1062	·0054	·0001	·0
1	·2684	·0397	·0015	·0
2	·3036	·1204	·0103	·0001
3	·2021	·2156	·0420	·0007
4	·0878	·2521	·1112	·0053
5	·0260	·2013	·2013	·0260
6	·0053	·1112	·2521	·0878
7	·0007	·0420	·2156	·2021
8	·0001	·0103	·1204	·3036
9	·0	·0015	·0397	·2684
10	·0	·0001	·0054	·1062

The results of calculations of the conductivities of mixtures for which $\rho_0 = 1$, and $\rho = \frac{1}{3\cdot 1}$ and $\frac{1}{16}$ respectively, are given in the following curves, along with the observed curves for mixtures of water and alcohol, and of vaseline and marble, and the curves for conductivity and resistivity following the linear law, for comparison. The calculation gives conductivities always below the observed values, a result which is due in part, and it may be entirely, to the neglect of the transverse transmission of heat from column to column of the model. The agreement is, however, sufficiently near to justify the statements that the thermal conductivity of a substance is not greatly modified when it enters as one constituent in a physical mixture, and that the thermal conductivity of a mixture depends directly on the amounts and conductivities of its constituents.

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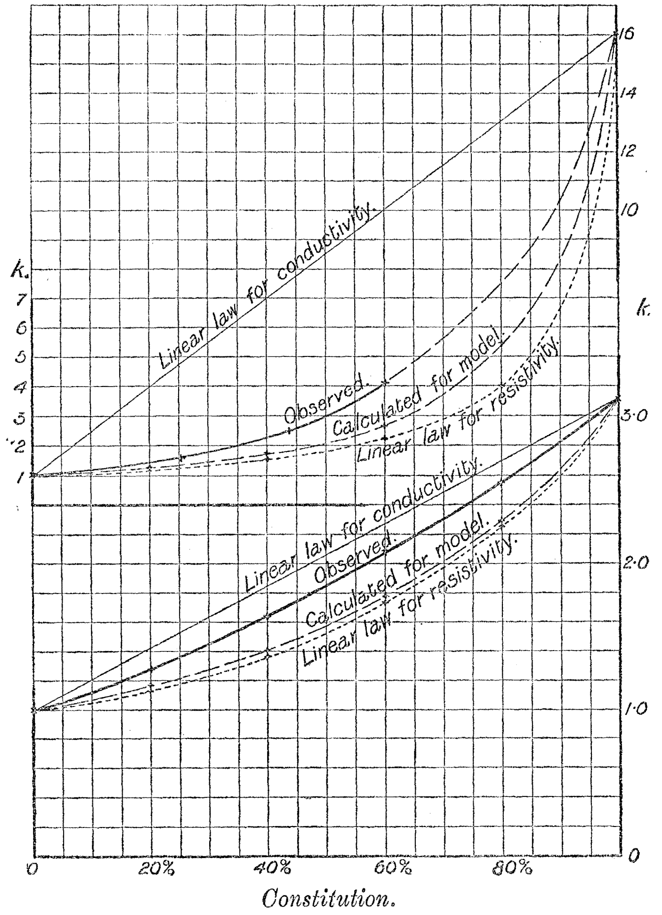
* 'Encyclopædia Metropolitana,' vol. 2, p. 486.



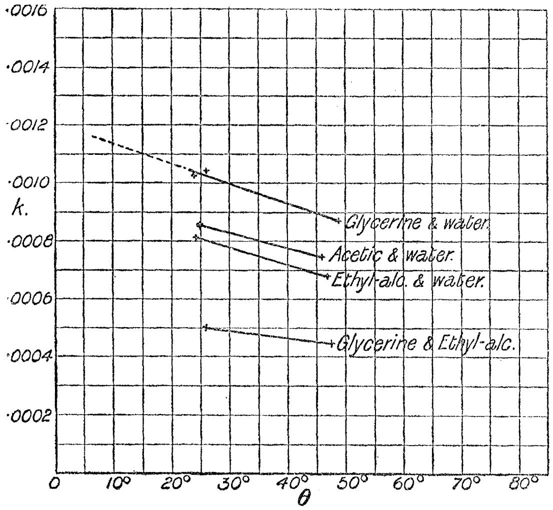
A reference to the values obtained for the thermal conductivities of solutions of a gas or a solid in water, will show that the above law does not apply to cases in which one constituent of the mixture changes its physical state on mixing. Further work is necessary before any law can be stated, but it seems probable that if the thermal conductivity of the gas or solid when liquefied were known and used as that of the material entering into solution, the above law would be found to cover solution as well as physical mixture.

PART V. CHANGE OF CONDUCTIVITIES OF MIXTURES WITH TEMPERATURE.

In order to determine the effect of temperature on the thermal conductivities of mixtures, experiments were made on several of the 50 per cent. mixtures of liquids mentioned in the preceding section. They were carried out with the enclosed apparatus, fig. 11, p. 419. The observations and results are given in the following tables and curves :—

Mixture.	θ_J.	U.	θ_U.	Reduced.		$\theta_M - \theta_L$.	θ_M.	B.	θ_B.	Temperature slope in glass.	Heat transmitted through glass.	$\cdot00026 v_U$.	$\cdot0017 v_M$.	Heat transmitted through liquid and ebonite.	Temperature slope.	Heat/slope.	Heat through liquid per unit slope.	k.	Temperature.
				U−M.	M−L.														
	°	ohms.	°	ohms.	ohms.	°	°	ohms.	°										°C.
50 per cent.* glycerine and water	17·44	3·45	26·74	·59	·63	1·68	25·17	1·10	20·44	5·59	·166	·002	·007	·157	13·2	·0119	·0110	·00102	24
	18·92	12·12	50·48	·562	·718	1·80	49·08	10·16	45·59	4·98	·154	·001	·005	·148	14·2	·0104	·0095	·00088	48
	18·76	3·77	28·89	·62	·66	1·75	27·25	1·78	23·57	5·84	·174	·001	·006	·167	13·8	·0121	·0112	·00104	26
50 per cent. acetic acid and water	18·20	3·40	27·36	·582	·733	1·955	25·81	1·06	21·09	5·51	·163	·002	·007	·154	15·4	·0108	·0091	·00084	25
	18·40	11·44	48·27	·52	·79	1·98	46·97	9·57	43·58	4·63	·144	·001	·005	·138	15·6	·00885	·0080	·00074	46
	18·74	3·38	27·83	·582	·727	1·94	26·28	1·23	22·07	5·51	·163	·002	·006	·155	15·3	·0101	·0092	·00085	25
	14·12	—·09	..	·704	·879	..	..	—·32	..	..	..	..	..	..	..	..	..	·00088	11
50 per cent. ethyl alcohol and water.	17·50	3·46	26·83	·591	·78	2·08	25·26	·98	20·17	5·59	·166	·002	·007	·157	16·4	·00957	·0087	·00081	24
	17·53	12·21	49·41	·562	·888	2·225	48·01	10·09	44·15	4·98	·154	·002	·006	·146	17·5	·00834	·0074	·00068	47
	17·34	3·63	27·12	·60	·80	2·14	25·52	1·80	22·23	5·70	·169	·001	·005	·163	16·8	·00970	·0088	·00081	24
	13·76	·23	..	·702	·957	..	..	—·22	..	..	..	..	..	..	..	..	..	·00079	11
50 per cent. glycerine and ethyl alcohol	17·36	3·93	28·95	·565	1·105	2·93	27·46	1·15	20·49	5·30	·158	·002	·010	·146	23·1	·00632	·0054	·00050	26
	18·00	12·11	49·62	·523	1·197	3·00	48·31	9·86	43·88	4·65	·145	·002	·007	·136	23·6	·00576	·0049	·00045	47
	17·84	4·30	29·40	·563	1·127	2·99	27·91	1·63	22·27	5·30	·158	·002	·008	·148	23·5	·00630	·0054	·00050	26

* By weight throughout.



Mixture 50 per cent. by weight of	k_{25}.	Mean percentage change per degree between 25° and 45° C.
Glycerine and water	·00103	— ·0063
Acetic acid and water	·00085	— ·0058
Ethyl alcohol and water	·00080	— ·0068
Glycerine and ethyl alcohol	·00050	— ·0050

It will be seen from this that the thermal conductivities of mixtures decrease with increase of temperature at roughly the same rate per cent. as their constituents.

STATEMENT OF RESULTS.

The preceding results may be summarised as follows :—

1. Solids which are not very good conductors of heat, in general decrease in conductivity with increase of temperature in the neighbourhood of 40° C. Glass is an exception to this rule.

2. Liquids in the neighbourhood of 30° C. follow the same law.

3. The conductivity of a substance does not invariably change abruptly at the melting point.

4. The thermal conductivity of a mixture lies between the conductivities of its constituents, and seems connected with the constitution and conductivities by a simple law.

5. Mixtures of liquids decrease in conductivity with increase of temperature in the neighbourhood of 30° C. at about the same rate as their constituents.