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1931 Proc. Phys. Soc. 43 581

(http://iopscience.iop.org/0959-5309/43/5/314)

THE DETERMINATION OF THERMAL CONDUCTIVITY AND ITS TEMPERATURE-VARIATION FOR MEDIUM CONDUCTORS

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Received May 7, 1931.

ABSTRACT. A plate method for the determination of thermal conductivity and its variation with temperature between 0 and 100° C. is described. Although specially adapted for medium conductors (of the order 0·001 to 0·02 c.g.s. units) such as rocks, it can be used for substances of lower conductivity.

§ 1. INTRODUCTION

In previous determinations of the thermal conductivities of poor or medium conductors by direct steady-state methods it has been customary to use specimens in the form of either a spherical shell, a hollow cylinder, or a plate or slab. While methods involving the use of a spherical shell or a cylinder possess certain advantages, yet on account of the ease with which specimens in the form of rectangular plates can be prepared and of the simplicity of construction of the necessary apparatus, the plate method has found most favour. It is with this method that the present paper deals.

If heat be supplied to one of the large faces of a rectangular plate at a constant rate, the determination of the thermal conductivity of the material of the plate involves the accurate measurement of two quantities, namely the heat-flow per unit area across the plate and the temperature-gradient normal to the surface to which heat is supplied. The rate at which energy is supplied can be measured with great accuracy when electrical heating is adopted, the chief difficulty being the estimation of the heat which is lost by conduction and radiation from the sides of the plate; this loss should therefore be reduced to a minimum or eliminated altogether. The losses can be made very small by using very thin plates*, a procedure which is satisfactory with poor conductors but becomes impracticable with medium conductors such as rocks owing to the small temperature-gradient. A thickness of at least 1 cm. is desirable, particularly if the specimen is not homogeneous for in that case a thin plate would not be a representative specimen. Thus by using thick plates increased accuracy in the measurement of temperature-gradient is secured at the expense of a greater lateral heat-loss. Guard-ring methods† have been used to eliminate the lateral heat-loss, such methods being ideal theoretically though they involve a complication of apparatus which it is the aim of the present method to avoid. In the present investigation a method has been used by means of which the losses can be reduced to about 5 per cent. or less, even with thick specimens, the

* Eg. E. Griffiths and G. W. C. Kaye, *Proc. R.S.* A, **104**, 71 (1923).
† E. Griffiths, "Heat Insulators," *Special Report No.* 35. *S.I.R.* (1929).

heat-loss or emissivity being determined by a subsidiary experiment with the same apparatus. Determinations of conductivities over the ranges 15 to 30° C. and 105 to 120° C. have been made for several substances, the values ranging from 0·002 to 0·014 c.g.s. units.

§2. DESCRIPTION OF APPARATUS

The system of plates in position in the constant-temperature enclosure is illustrated in figure 1. In order to ensure symmetry in the heat-flow two similar specimens were used, one on either side of the hot plate. The latter consisted of a unit made by sandwiching two nichrome-wire-asbestos heating mats, connected in parallel, between two brass plates each 15 cm. × 14 cm. × 1 cm. which are screwed together tightly. Each mat had a resistance of 100 ohms. Two mats in parallel were used for reasons of symmetry, their similar sides facing each other. The mats were insulated from the brass plates by sheets of mica and from each other by a wad of asbestos paper. On the outer faces of the specimens are mounted two similar channelled brass castings, each 15 cm. × 14 cm. × 1·5 cm., through which a rapid stream of water can circulate so as to carry away the heat transmitted through the specimens. These will be referred to as the cold plates.

The temperatures of the cold faces of the specimens being in this way kept practically constant and equal to that of the enclosure, the mean excess temperature of the specimens is never allowed to become very high, whereas the heat-supply and consequently the temperature-gradient can be made quite large. Such a method, which can be called "calorimetric" (as distinct from an "emissivity" method, which differs in having no water-circulation through the cold plates and is similar in principle to the classical method of Lees*), has marked advantages in permitting large values of the energy supplied (say 50 to 100 watts) and of the temperature-gradient (say 5 to 20 degrees/cm.) and thus increasing the percentage accuracy with which these quantities can be measured. As the mean excess temperature of the specimens above that of the enclosure is very much less in the calorimetric method than in the emissivity method for the same heat-supply, the heat-loss (which is approximately proportional to the excess temperature) will also be very much less. The following figures, taken from tables 1 and 2, afford an excellent comparison of the two methods; it will be seen that the heat-loss from the sides of the specimens amounts to 31 per cent. of the heat generated in the heating coil in one case, but only 3 per cent. in the other.

	Emissivity method	Calorimetric method
Energy W supplied to coil	10·19	52·41 watts
Loss w_1 from sides of hot plate	1·44	1·40 ,,
Loss w_2 from sides of specimens	3·18	1·55 ,,
Mean flow $\overline{W}$ through specimens (i.e. $W - w_1 - w_2/2$)	7·16	50·23 ,,
Mean temperature θ_1 of hot face	25·70° C.	27·93° C.
Mean temperature θ_2 of cold face	23·61° C.	12·49° C.
Mean temperature drop $(\theta_1 - \theta_2)$	2·09° C.	15·44° C.
Thermal conductivity	$5·33 \times 10^{-3}$	$5·06 \times 10^{-3}$ c.g.s.

* *Phil. Trans.* A, **191**, 399 (1898).

An experiment performed without water-circulation through the cold plates gives the value of the emissivity which is used in calculating the heat-losses in the main (calorimetric) experiment. Since these losses are small, the emissivity is not

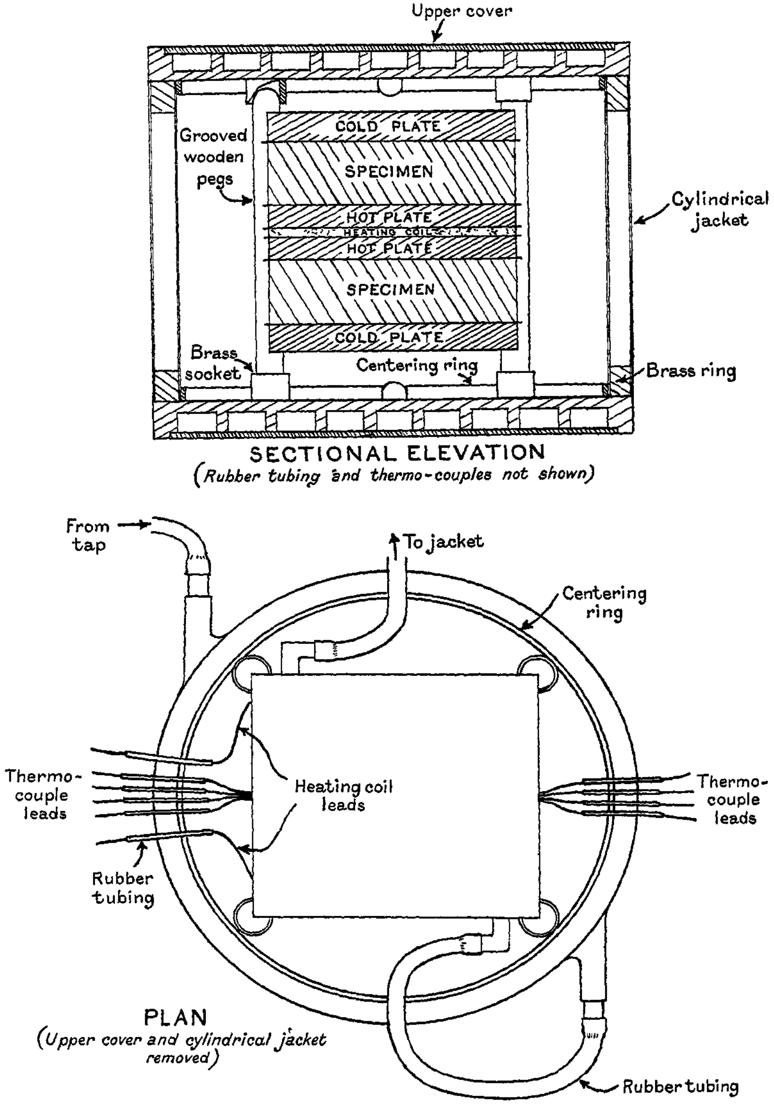

Fig. 1.

required to a high order of accuracy, an error of 10 per cent. in its value producing an error of less than 0·5 per cent. in the value of the conductivity. It is rather surprising that the value of the conductivity deduced by the emissivity method should

differ by only 5 per cent. from the more reliable value given by the calorimetric method in spite of the smallness of the temperature-drop and the uncertainty in the value of the relatively large heat-loss in the former method. Assuming for the moment that no errors are introduced on this account, the discrepancy between the two values can only be explained by the fact that the usual assumption with regard to the effective heat-flow through the specimen is not justified. The assumption in
$\overline{W}$ question is that the effective heat-flow $\overline{W}$ is the mean of the heat $(W - w_1)$ which enters the hot face and of that $(W - w_1 - w_2)$ which reaches the cold face, i.e.

$$\overline{W} = W - w_1 - w_2/2.$$

For example, if the effective flow is given by the expression

r
$$\overline{W} = W - w_1 - rw_2,$$

where $0 < r < 1$, the appropriate value of r which in the example quoted will make the values of the conductivity agree is 0·63, the values then becoming $5{\cdot}02 \times 10^{-3}$ and $5{\cdot}04 \times 10^{-3}$ respectively, the former being reduced by 6 per cent. and the latter by only 0·5 per cent. The difference between the values of the conductivity obtained by the two methods was always about 5 per cent. so that the error, if any, involved in taking the value of r as $\frac{1}{2}$ will only be 0·5 per cent. of the conductivity as deduced by the calorimetric method. In short, the experimental results lead one to suppose that the effective heat-flow should be given by

$$\overline{W} = W - w_1 - rw_2,$$

where $\frac{1}{3} < r < \frac{2}{3}$, the error in the conductivity due to the uncertainty in the correct value of r never exceeding 0·5 per cent.

The heating current is supplied by a battery of accumulators, the wattage being calculated from the resistance of the coil and the potential-difference between its terminals as measured with a calibrated voltmeter. The wattage can be measured in this way to the same order of accuracy as the other quantities, the necessity of using a more elaborate potentiometer method being thus dispensed with.

Measurement of temperature. It is important that the temperatures be measured at two points a known distance apart along the lines of heat-flow in the specimen. The practice of embedding thermocouples in the specimen itself is undesirable from the point of view of the inevitable distortion of the lines of heat-flow produced by the material used to cement the couples in place. It is also inadvisable to measure the temperatures of the hot and cold plates on the assumption that these give the temperatures of the specimen surfaces, particularly when the latter are hard or uneven, for then the thermal contact is poor and it is preferable to use thermocouples in direct contact with the surfaces, as pointed out by Griffiths*. The thermal contact can be improved by using between the surfaces a cementing material, the thickness of which should be very small in comparison with the thickness of the specimen, a condition difficult to fulfil with thin plates. With thick specimens (1 cm. or more) the accuracy of measurement of temperature-gradient is increased, and it

* *Loc. cit.*, p. 14.

is not necessary to adopt special methods of ensuring perfect plane parallelism of the faces or of measuring the thickness.

In the present work the temperatures at the centres of the actual faces were measured by means of thermocouples in good thermal contact with the faces, the couples being in the form of very thin strips sandwiched between the specimens and the hot and cold plates. With brass plates of the thickness used here the temperature is uniform over the surface to within a short distance of the edges. The thermocouples were made by hard-soldering together 28-gauge copper and constantan wires and rolling them out to form a strip about 15 cm. long and 0·03 mm. thick, with the junction in the centre. Latterly constantan-manganin couples were used in preference to copper-constantan couples owing to the fragility of thin copper strip, the e.m.f. per degree being only slightly less. There is also the additional advantage that the temperature-coefficients of resistance of both constantan and manganin are small, so that the galvanometer deflection per microvolt has practically the same value at 0° C. as at 100° C. Readings of the e.m.f. were made with a slide-wire potentiometer adjusted to give a potential drop of 1 microvolt per mm. down the wire; the galvanometer, which was of the moving coil type, had a voltage-sensitivity of 2·5 divisions per microvolt. The e.m.f. could easily be measured to 1 microvolt, corresponding to a temperature of about 0·02° C. Subsequently the slide-wire potentiometer was replaced by a thermoelectric potentiometer of the Cambridge Scientific Instrument Co. The e.m.f./temperature relations were obtained experimentally with sample couples over the range 0° to 100°, one junction being in melting ice and the other in a vacuum flask containing water, the temperature of which could be controlled by a small heating coil and measured with a platinum resistance thermometer. If E represents the e.m.f. of the couple in microvolts for a hot-junction temperature of t° C. the parabolic equation

E

t

$$E = at + bt^2,$$

a, b

fits the observed values closely over the range 0° to 100° and can safely be extrapolated to 130°, the values of the constants being

$$a = 38{\cdot}5, \quad b = 0{\cdot}0425 \text{ for copper-constantan,}$$
$$a = 35{\cdot}6, \quad b = 0{\cdot}0412 \text{ for constantan-manganin.}$$

The e.m.f. for $t = 100$ is practically the same for all couples provided the latter be made from wire taken from the same two reels; in one case, for example, five constantan-manganin couples had the following e.m.f.'s: 3962, 3963, 3963, 3965 and 3967 microvolts. In calibrating the couples used in the apparatus it is therefore sufficiently accurate to determine the e.m.f.'s at 100° and apply a proportionate correction on the appropriate parabolic formula. It has been shown by Adams* that the relation for a copper-constantan couple over an extended temperature-range (0° to 350° C.) is accurately given by the formula

$$E = 74{\cdot}672t - 13892\,(1 - e^{-0{\cdot}00261t}).$$

* *J. Amer. Chem. Soc.* **36**, 65 (1914).

Over the range of temperatures used in the present work (0°–130°) the simpler parabolic formula gives values of the e.m.f. which agree with those obtained from the above formula to within 2 or 3 microvolts.

The four thermocouples are insulated from the hot and cold plates by thin sheets of mica 0·05 mm. thick and of area slightly greater than that of either plate. These sheets must make good thermal contact with the hot and cold plates and with the surfaces of the specimens. A suitable substance for this purpose is British pitch, which is sufficiently fluid at 100° to flow over the surface and sufficiently viscous to be retained between the plates at 130°, the highest temperature reached. The four mica sheets are first attached to the surfaces of the hot and cold plates by means of the pitch, layers of pitch are then formed on the surfaces of the mica sheets; and the whole system of plates, including the two specimens with the thermojunctions in place, is mounted in a framework to prevent slipping. Steam is now circulated through the cold plates, and under the pressure of a 28-lb. weight the surplus pitch is gradually squeezed out until very thin layers exist between the surfaces. Owing to the high viscosity of pitch even at 100° this may take a considerable time, but it is inadvisable to expedite matters owing to the danger of creating small air pockets in the layers of pitch.

The constant-temperature enclosure. In order to make the external conditions definite, and to investigate the thermal conductivity above 100° C., the apparatus must be placed in a constant-temperature enclosure. The latter consists of three portions, a hollow cylindrical jacket through which water or steam may circulate, and an upper and a lower cover channelled for water- or steam-circulation in the same way as the cold plates of the apparatus. Through the lower of the brass rings which form the ends of the cylindrical jacket are bored four small holes on either side for the passage of the thermocouple and heating-coil leads, and two ⅜-in. holes, one on either side, for the passage of rubber tubing carrying the water circulating through the lower cold plate. A similar pair of holes through the brass ring at the upper end of the cylindrical jacket suffices for the rubber tubing connected to the upper cold plate. On the inner surface of the lower cover are soldered four brass sockets, the centres of which are at the corners of a rectangle of the same size, 15 cm. × 14 cm., as the faces of the system of plates. Four ⅜-in. wooden rods are fixed in these sockets, the rods being grooved along their length to within an inch of their base so as to support the system of plates at the corners, thus preventing any sliding of one plate over another.

§ 3. EXPERIMENTAL PROCEDURE

In carrying out a determination at room temperature, a rapid stream of water from the tap is passed through the lower cover, lower cold plate, cylindrical jacket, upper cold plate and upper cover in the order named. The heating current is then established and after the lapse of an hour the e.m.f.'s of the four thermocouples are measured until constant values are indicated. Temperature-readings are obtained in this way for different values of the potential-difference between the heating coil terminals. The stream of water is sufficiently rapid to give, for a supply of 100 watts to the heating coil, a rise of temperature of not more than 0·4° C. in passing through the cold plate, this rise of temperature being observed by means of mercury thermometers inserted in the circulating medium just before and after passage through one of the cold plates. A series of temperature-readings having been obtained for different values of the heating current, a series of emissivity readings is made over the same temperature-range by disconnecting the rubber tubing from the cold plates, the water-flow being through the jacket and covers only. Much smaller values of the heating current suffice in this case, but the realization of steady conditions is prolonged to about 8 to 10 hours, instead of one hour as in the calorimetric method.

The procedure was similar in making determinations of the conductivity above 100° C., except that steam was passed through the system in the reverse order, i.e. downwards instead of upwards, any tendency to superheat being thus avoided; the steam was then condensed and returned to the boiler.

§4. THEORY OF THE METHOD

Determination of the emissivity. Let

W be the energy supplied to heating coil in watts; W
d_h the thickness of the hot plate in cm.; d_h
d_c the thickness of each cold plate in cm.; d_c
d_s the mean thickness of the specimen in cm.; d_s
p the perimeter of the specimen in cm.; p
A the area of face of the specimen in cm.^{2}; A
θ_1 the mean temperature of the hot faces in degrees C.; θ_1
θ_2 the mean temperature of the cold faces in degrees C.; θ_2
ϕ the temperature of the enclosure in degrees C.; ϕ
h the emissivity in watts/cm.^{2}-degrees; and h
K the thermal conductivity in c.g.s. units. K

Then it follows that in the steady state

$$W = h\left\{pd_h(\theta_1-\phi)+2pd_s\left(\frac{\theta_1+\theta_2}{2}-\phi\right)+2(pd_c+A)(\theta_2-\phi)\right\},$$

from which the value of h at a mean temperature of $(\theta_1+\theta_2)/2$ can be determined. The assumption is here made that h is the same for all the surfaces and is independent of the temperature. As the difference between θ_1 and θ_2 is never more than 3 or 4 degrees in this experiment the latter assumption is justified. The first assumption is not strictly legitimate even if the different surfaces be made similar by varnishing, so that the above equation gives only a rough average value for the emissivity. As was pointed out previously, however, a comparatively large error on this account influences the value of the conductivity to only a small extent.

K The approximate value of the conductivity K as given by this method is

$$K = \overline{W} d_s / 2A\,(\theta_1 - \theta_2) \times 4{\cdot}18,$$

$\overline{W}$ where $\overline{W}$, the effective flow through the specimens, is given by

$$\overline{W} = W - hpd_h\,(\theta_1 - \phi) - hpd_s\{(\theta_1 + \theta_2)/2 - \phi\}.$$

Determination of the thermal conductivity by the calorimetric experiment. If, as before, θ_1 and θ_2 represent the mean temperatures of the hot and cold faces respectively in the calorimetric experiment, the hot plate will be at an excess temperature of $(\theta_1 - \theta_2)$ above that of the enclosure, and the specimens will be at an excess temperature of $(\theta_1 - \theta_2)/2$ approximately, since the temperatures of the cold faces and of the enclosure are practically the same.

The effective flow is therefore given by

$$\overline{W} = W - h_1 pd_h\,(\theta_1 - \theta_2) - h_2 pd_s\,(\theta_1 - \theta_2)/2,$$

h_1, h_2 where h_1 is the emissivity at a temperature θ_1, and h_2 is the emissivity at a temperature $(\theta_1 + \theta_2)/2$, these values being given by the emissivity experiment.

The thermal conductivity is, as before, given by

$$K = \overline{W} d_s / 2A\,(\theta_1 - \theta_2) \times 4{\cdot}18,$$

at a mean temperature $(\theta_1 + \theta_2)/2$.

§ 5. SPECIMEN OF OBSERVATIONS

As an example of the method the observations are given in some detail for slate

$$d_h = 2{\cdot}35 \text{ cm.},$$
$$d_c = 1{\cdot}565 \text{ cm.},$$
$$d_s = 2{\cdot}795 \text{ cm.},$$
$$p = 58{\cdot}7 \text{ cm.},$$
$$A = 215{\cdot}0 \text{ cm.}^2.$$

Table 1. Values of the emissivity.

W (watts)	θ_1 (° C.)	θ_2 (° C.)	ϕ (° C.)	$(\theta_1 + \theta_2)/2$ (° C.)	h (watts/cm.^{2}-degree)
5·73	19·31	18·19	9·85	18 75	$6{\cdot}15 \times 10^{-4}$
6·98	21·88	20·52	10·50	21 20	$6{\cdot}23 \times 10^{-4}$
8·94	24·21	22·49	10·25	23·35	$6{\cdot}53 \times 10^{-4}$
10·19	25·70	23·61	9·55	24 65	$6{\cdot}47 \times 10^{-4}$
11·91	28·45	25·97	9·90	27·21	$6\ 60 \times 10^{-4}$
14·78	32·33	29·24	10·05	30·79	$6{\cdot}84 \times 10^{-4}$

Values obtained above 100° C. ranged from $9{\cdot}34 \times 10^{-4}$ at a mean temperature of 108·62° C. to $10{\cdot}72 \times 10^{-4}$ at a mean temperature of 127·51° C. By plotting emissivity against mean temperature graphs are obtained from which the appropriate value of h can be read off in deducing the losses in the main experiment.

Table 2. Values of the thermal conductivity.

W (watts)	θ_1 (° C.)	$(\theta_1 - \theta_2)$ (° C.)	w_1 (watts)	w_2 (watts)	$\overline{W}$ (watts)	$(\theta_1 + \theta_2)/2$ (° C.)	$K \times 10^3$ (c.g.s.)
32·87	22·76	9·71	0·85	0·96	31·54	17·90	5·052
35·63	23·20	10·49	0·92	1·04	34·19	17·96	5·067
47 95	27·53	14·02	1·27	1·41	45·97	20·52	5·100
52·41	27·93	15·44	1·40	1·55	50·23	20·21	5·060
63·16	31·52	18·62	1·74	1·92	60·46	23·21	5·049
69·76	33·22	20·47	1·94	2·12	66·76	23·23	5·072
74·54	35·32	21·92	2·10	2·28	71·30	24·36	5·057
80·46	37·13	23·64	2·31	2·48	76·91	25·31	5·059
93·89	41·00	27·53	2·76	2·93	89·66	27·23	5·064
104·0	44·33	30·51	3·14	3·28	99·22	29·07	5·058
109·2	46·00	32·12	3·43	3·50	104·0	29·94	5·035
115·7	47·99	33 98	3·60	3·74	110·2	31·00	5·044

The following values of $K \times 10^3$ were obtained for mean temperatures ranging from 105·43° C. to 113·88° C., the values of W ranging from 28·15 watts to 73·96 watts, and $(\theta_1 - \theta_2)$ from 8·76° C. to 22·82° C.:

4·694, 4·684, 4·697, 4·690, 4·694, 4·670, 4·679, 4·672, 4·681, 4·702, 4·671, 4·690.

The above values of the conductivity are plotted against the mean temperature in figure 2.

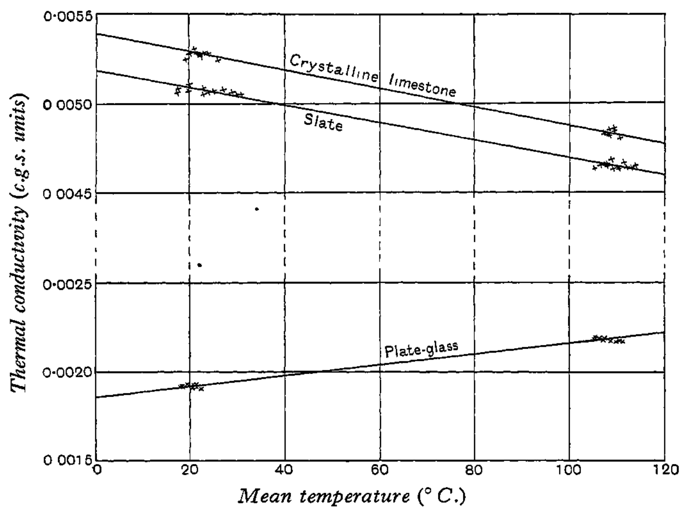

Fig. 2.

On the assumption that a linear relation

$$K_\theta = K_0 (1 + \alpha\theta),$$

K_θ, K_0, α

holds over the range 0° C. to 130° C. the following values are obtained:

$$K_0 = 0{\cdot}00517 \text{ c.g.s. units,}$$
$$\alpha = -0{\cdot}00085.$$

It will be noted that for this specimen the lateral loss amounts to 3·4 per cent. of the total heat supplied at room temperature. At 100° C. the loss is nearly 5 per cent. By cutting down the plates to a thickness of $\frac{1}{4}$ in. it would be possible to reduce the lateral loss to 1 per cent., while still maintaining an accurately measurable temperature-difference. In spite of the comparatively large heat-loss the values obtained show a fair consistency, as will be seen from the table; the consistency is even greater in the case of plate glass, for which, owing to its small thickness ($\frac{1}{4}$ in.), the percentage loss is less. It may be remarked that the determinations at steam temperatures were generally more erratic than those at room temperature.

§6. SUMMARY OF RESULTS

The following substances were investigated: plate glass, slate, crystalline limestone and quartzite. The quartzite was obtained from South Africa; the sources of the limestone and the slate are not known. The specimens of slate show evidence of laminations in planes parallel to the largest faces (i.e. at right angles to the direction of heat-flow).

The values of the thermal conductivity at 0° C. and the temperature-coefficient are given in table 3.

Table 3.

Substance	Density (gm./cm.^{3})	K_0 (c.g.s.)	α
Plate glass	2·55	0·001845	+ 0·00168
Slate	2·78	0·00517	− 0·00085
Crystalline limestone	2·70	0·00539	− 0·00095
Quartzite	2·95	0·01493	− 0·00163

Except in the case of plate glass, values obtained by other investigators vary considerably. These variations are undoubtedly due in part to differences in the composition of substances of the same name which may have been quarried from widely separated localities.

For plate glass Meyer* obtained the value 0·00179 at 12·5° C., while the value given by Niven and Geddes† (0·001923 at 20° C.) agrees with the author's.

Previous values for slate are considerably lower than the above value; Lees and Chorlton‡ give 0·00357 at 94° C. while Herschel, Lebedour and Dunn§ obtained a value of 0·0034 perpendicular to the cleavage planes, the value in a direction at right angles being much higher. The low values could be explained if the specimens

* *Wied. Ann.* **34**, 596 (1888).

† *Proc. R.S.* A, **87**, 535 (1912).

‡ *Phil. Mag.* **41**, 495 (1896).

§ *Brit. Ass. Report*, **49**, 58 (1879).

of slate used by these observers were more markedly laminar than those used in the present work.

Limestones and marbles vary considerably, as judged by the wide range of values of conductivity; Poole* gives values ranging from 0·0046 to 0·0057 at 40° C. and 0·0039 to 0·0049 at 100° C., those at the lower temperature being in substantial agreement with the determinations of Herschel, Lebedour and Dunn†. Values as high as 0·007‡ have been obtained for marble.

The comparatively small number of determinations of temperature-coefficients shows even greater discrepancies between the values obtained by different observers. According to the present work slate, limestone and quartzite possess negative coefficients, and this result is in agreement with those obtained for the majority of rocks. In connexion with the positive value obtained for plate glass it may be noted that Lees§ gives a value of + 0·0025 for window glass.

§ 7. ACKNOWLEDGMENT

The above investigation was suggested by the late Prof. H. L. Callendar, F.R.S., from whose constant interest and advice the author derived much valuable help, which he gratefully acknowledges.

* *Phil. Mag.* **24**, 45 (1912).
† *Loc. cit.*
‡ A. Eucken, *Ann. d. Phys.* **34**, 185 (1911).
§ *Loc. cit.*