On the Thermal Conductivities of Mixtures and of their Constituents

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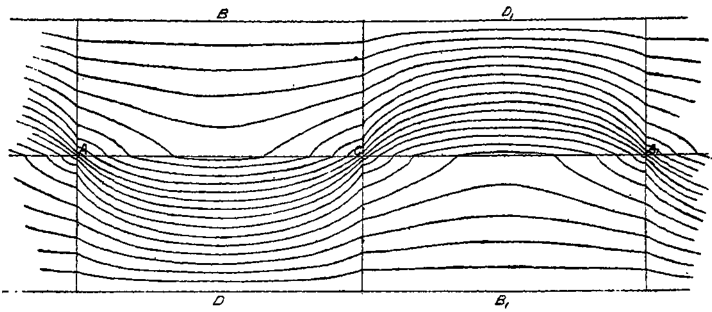
through the centres of the squares parallel to their sides is obtained. The conductivity of the medium for this flux will be readily seen to be given again by the formula

$$k=\sqrt{k_1k_2}.$$

The equipotential lines (or the stream-lines) for a strip of the medium, when one constituent conducts six times as well as the other, are shown in fig. 6.

Fig. 6.



Since there are four directions of flow in the medium for which the conductivity has the above value, the conductivity of the medium when fine-grained will have the same value for a flux in any direction; *i. e.* equation (4) gives the conductivity of a compound medium in the general case where the constituents are present in the form of long prisms with their axes perpendicular to the planes of flow.

IV. *On the Thermal Conductivities of Mixtures and of their Constituents.* *By* Charles H. Lees, *D.Sc.**

Those physicists who have endeavoured to express the thermal conductivities of physical mixtures in terms of the conductivities of their constituents, and the amount of each present, have made use of the formulæ

$$k=\frac{p_1k_1+p_2k_2}{p_1+p_2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{k}=\frac{p_1\frac{1}{k_1}+p_2\frac{1}{k_2}}{p_1+p_2}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Read November 24, 1899.

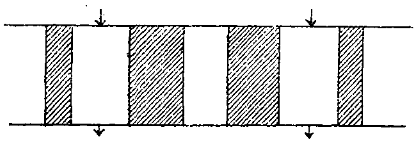
where k_1 and k_2 are the conductivities of the constituents, and p_1 and p_2 either the masses or the volumes of each present. Paalhorn, Winkelmann, and Schott, in their paper on the conductivities of glasses *, used the first form with the p's the masses of the constituents present; but Winkelmann has recently recalculated the results †, using the second form, with the p's the volumes of the constituents present, and found a better agreement than formerly.

Focke ‡ uses the first formula, with the p's the masses, to represent his own results on the conductivities of various kinds of glass. Both theory and experiment §, however, point to the conclusion that it is the proportion by volume which ought to be used in such calculations; and I shall confine myself in what follows to the consideration of the proportions by volume, calculated on the assumption that the mixture is simply a physical mixture, and is formed without contraction. Under these conditions the formula

$$k = \frac{p_1 k_1 + p_2 k_2}{p_1 + p_2}$$

corresponds to the constituents being distributed in the space between the two parallel isothermal surfaces through which the heat enters and leaves the medium, in the form of right prisms with their axes perpendicular to these surfaces, thus :-

Fig. 1.



and the formula

$$\frac{1}{k} = \frac{p_1 \frac{1}{k_1} + p_2 \frac{1}{k_2}}{p_1 + p_2}$$

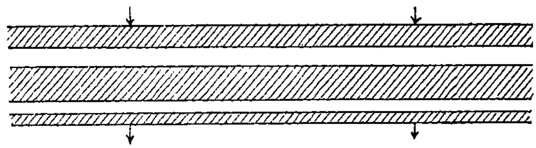
to their being distributed in layers parallel to the isothermal surfaces, thus :—

* Wied. *Ann.* li. p. 738 (1894).

† *Ibid.* lxvii. p. 160 (1899). ‡ *Ibid.* lxvii. p. 155 (1899).

§ Lees, Phil. Trans. Royal Society, cxci. p. 433 (1898); *ante*, p. 70.

Fig. 2.

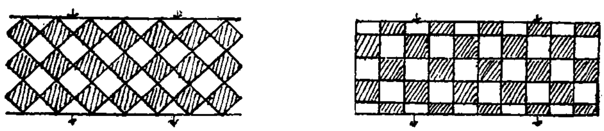


It has been recently shown * that the formula

$$\log k = \frac{p_1 \log k_1 + p_2 \log k_2}{p_1 + p_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

corresponds to a prismatic distribution which, in the case of equal volumes of the constituents being present, is represented in section thus:—

Fig. 3.



As one cannot assume that one of these three distributions is more likely than another to represent the actual facts, I propose to apply each of the three formulæ to the calculation of the conductivities of the mixtures of solids and liquids experimented on by G. Wiedemann †, Henneberg ‡, and myself §, and compare the results of the calculations with the values found experimentally.

It will be noticed that the conductivities determined for successive equal increments of one constituent, correspond for the first formula to the successive terms of an arithmetic, for the second to the terms of a harmonic, and for the third to those of a geometric series, the first and the last terms of the three series being the same. The third formula will therefore give a value for the conductivity of a given mixture between the values given by the first and second formulæ. In the tables which follow the values calculated by the three formulæ (1), (2), and (3) are referred to as "mean conductivity," "mean resistivity," and "mean logarithmic" respectively.

* Lees, *ante*, pp. 72–73.

† G. Wiedemann, Pogg. *Ann.* cviii. p. 393 (1859).

‡ Henneberg, Wied. *Ann.* xxxvi. p. 146 (1889).

§ Lees, Phil. Trans. Royal Soc. cxci. p. 399 (1898).

Tin-Bismuth Alloy * (Wiedemann).

Composition by volume.	k observed, Ag=100.	k calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Sn	15·2						
„ 20 p. c. Bi	10·1	12·5	+ 24	6·1	−40	9·9	− 2
„ 42·7 p. c. Bi ...	5·6	9·5	+ 70	3·6	−36	6·1	+11
„ 69·1 p. c. Bi......	2·3	5·9	+156	2·5	+ 8·7	3·5	+52
Bi	1·8						

Dilute Ethyl Alcohol (Henneberg).

Composition by volume.	k obs.	k calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water	100						
„ 12·4 p. c. Ethyl Alc....	91	91·3	+ 3	78·0	−14	86·1	− 5·4
„ 24·5 „ „ ...	81·4	82·9	+ 2	63·8	−22	74·5	− 8·5
„ 36·1 „ „ ...	73·1	74·8	+ 2	54·4	−26	64·9	−11
„ 47·3 „ „ ...	64·6	66·9	+ 4	47·7	−26	56·8	−12
„ 57·8 „ „ ...	54·6	59·6	+ 9	42·7	−22	50·0	− 8
„ 67·7 „ „ ...	47·6	52·7	+11	38·9	−18	44·4	− 7
„ 76·9 „ „ ...	41·7	46·3	+11	35·9	−14	39·7	− 5
„ 85·4 „ „ ...	37·5	40·3	+ 7	33·5	−11	35·9	− 4
„ 93·2 „ „ ...	32·1	34·9	+ 9	31·6	− 2	32·7	− 2
Ethyl Alcohol	30·1						

Water and Glycerine.

Water	·00140						
„ 20·8 p. c. Glycerine ...	119	125	+ 5	116	−3	121	+2
„ 44·2 „ „ ...	101	109	+ 8	97	−4	103	+2
„ 70·4 „ „ ...	81	91	+12	82	−1	86	+6
Glycerine	70						

Water and Ethyl Alcohol.

Water	·00149						
„ 30 p. c. Alcohol	104	118	+13	99	− 5	105	+1
„ 58 „ „	79	90	+14	66	−16	76·4	−3
„ 81 „ „	59	60	+12	54	− 8	58·5	−1
Ethyl Alcohol	47						

* Wiedemann's copper-zinc results appear to exclude this alloy from the class of physical mixtures.

Water and Acetic Acid.

Composition by volume.	k obs.	k calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water	·00149						
„ 24 p. c. Acetic Acid	118	124	+ 5	94	−20	110	−7
„ 48·7 „ „	88	97	+10	68	−23	82	−7
„ 74 „ „	64	71	+11	53	−17	59	−8
Acetic Acid	43						
Water and Methyl Alcohol.							
Water	·00148						
„ 28·8 p. c. Meth. Alc.	111	120	+ 8	97	−13	109	−2
„ 58·0 „ „	80	92	+15	71	−11	81	−1
„ 80·7 „ „	63	70	+11	59	− 6	64	−1
Methyl Alcohol	52						
Ethyl Alcohol and Glycerine.							
Ethyl Alcohol	·00044						
„ „ 17·4 p. c. Glyc.	43	49	+14	47	+9	48	+12
„ „ 38·7 „ „	50	54	+ 8	51	+2	53	+ 4
„ „ 65·3 „ „	56	61	+ 9	58	+4	60	+ 7
Glycerine	70						
Methyl Alcohol and Ethyl Alcohol.							
Methyl Alcohol	·00052						
„ „ 25 p.c. Ethyl Alc.	5	505	+1	505	+1	505	+1
„ „ 50 „ „	47	49	+4	49	+4	49	+4
„ „ 75 „ „	46	475	+3	47	+2	475	+3
Ethyl Alcohol	46						
Vaseline and Marble.							
Vaseline	·00044						
„ 25 p. c. Marble	63	210	+233	57	−10	88	+40
„ 43 „ „	108	330	+206	74	−31	145	+34
„ 60 „ „	179	444	+149	102	−43	234	+31
Marble	710						
Lard and Zinc Sulphate.							
Lard	·00047						
„ 23·8 p. c. $ZnSO_4$	59	60	+ 2	56	− 5	61	+3
„ 37·5 „ „	74	84	+14	63	−15	72	+3
„ 55·5 „ „	84	101	+20	75	−11	88	+5
Zinc Sulphate	145						

Without endeavouring to express the relative values of the three formulæ numerically, we may arrange the three in order of merit for each mixture as follows :—

	Order of merit of calculated Values.		
	Best.	Middle.	Worst.
Water and Ethyl Alcohol (Henneberg)	Conductivity. Logarithm.	....	Resistivity.
Water and Ethyl Alcohol (Lees)	Logarithm.	Resistivity.	Conductivity.
Water and Glycerine	Resistivity.	Logarithm.	Conductivity.
Water and Acetic Acid ...	Logarithm.	Conductivity.	Resistivity.
Water and Methyl Alcohol.	Logarithm.	Resistivity.	Conductivity.
Ethyl Alcohol and Glycerine......................	Resistivity.	Logarithm.	Conductivity.
Ethyl Alcohol and Methyl Alcohol	Resistivity.		Conductivity. Logarithm.
Tin and Bismuth (Wiedemann)	Logarithm.	Resistivity.	Conductivity.
Vaseline and Marble	Resistivity.	Logarithm.	Conductivity.
Lard and Zinc Sulphate ...	Logarithm.	Resistivity.	Conductivity.

From this it will be seen that the formula

$$k = \frac{p_1 k_1 + p_2 k_2}{p_1 + p_2}$$

represents the observed results worst, and that of the other two the formula

$$\log k = \frac{p_1 \log k_1 + p_2 \log k_2}{p_1 + p_2}$$

is somewhat better than

$$\frac{1}{k} = \frac{p_1 \frac{1}{k} + p_2 \frac{1}{k_2}}{p_1 + p_2}.$$

The representation of the observed facts which even the best of the three gives is, however, only rough. As a rule the mean resistivity formula gives too low, and the mean logarithmic formula too high, values for the conductivity of each mixture. Now the conductivity of a compound built up of two materials, as in fig. 3, but with the same structure repeated in a plane perpendicular to that of the drawing, *i. e.* consisting of cubes of the two media, will be greater than that of the prisms of fig. 3, and will therefore deviate more from the value of the conductivity found experimentally than does that given by the logarithmic formula. Hence it seems unnecessary to attempt an accurate calculation of the conductivity of the mixture of cubes. Since the deviations from the calculated values found in the cases considered in the above tables also appear to differ in character from one mixture to another, it may be concluded that the thermal conductivity of a mixture is not completely determined by the conductivities of its constituents, and by the volume of each constituent present.

The attempts which have hitherto been made to represent the thermal conductivity of glass as a function of its composition and of the unknown conductivities of its constituents, must therefore be considered as not justified by our knowledge of the behaviour of mixtures of substances the conductivities of which are known.

The formula expressing the conductivity of a mixture in terms of its composition and the conductivities of its constituents, must then contain at least one quantity dependent on the characters of the two constituents, and three of the calculated values of the conductivity may be made to coincide with the observed values. There are many empirical formulæ which under these conditions give values that agree fairly well with the intermediate observations; and although I have found the formula

$$k^n = \frac{p_1 k_1^n + p_2 k_2^n}{p_1 + p_2}, \quad \ldots \ldots \quad (4)$$

where n is an arbitrary constant, on the whole satisfactory, the material at our disposal for testing the relative values of the various empirical formulæ which might be suggested, is not yet sufficient to warrant the selection of any one of them as the best representation of the thermal conductivity of a mixture.

The result of this examination may then be summed up as follows :—

Of the three values for the conductivity of a mixture calculated from the mean conductivity, mean resistivity, and mean logarithmic formulæ, that from the mean conductivity is most unsatisfactory, and that from the mean logarithmic formula least unsatisfactory. The logarithmic formula gives in general too high, and the resistivity formula too low a value for the conductivity.

The conductivity of a mixture appears not to be dependent solely on the volume and conductivity of each constituent present.

The empirical formula (4) gives a fair representation of the observations in the preceding tables.

Discussion.

Mr. Appleyard pointed out that it was frequently of importance to be able to calculate the specific resistance of a mixture of dielectrics from the known specific resistances of the components. He had attempted to do this by means of the old formulæ, but with only approximate success ; the one gave a result too low, and the other a result too high. He expected improved results by applying Dr. Lees' formula to such a case. Moveover, from the nature of the problem, Dr. Lees' formula should enable the specific capacity of a dielectric mixture to be calculated from the specific capacities of its components ; this was of great practical importance in the manufacture of cable-core.

Mr. Campbell said that the difference between the calculated and observed results might be due to the thermoelectric properties of the materials. Lord Rayleigh had observed that the high resistivity of alloys might be due to a back E.M.F. due to the Peltier effect at the junction of dissimilar metals. Mr. Campbell said that he had measured the resistances of ferro-nickel both with direct and alternative currents, and found them the same in the two cases, although iron and nickel are widely apart on the thermoelectric diagram.