CONDUCTIVITIES AND THERMO-ELECTRIC POWERS OF BISMUTH-TIN ALLOYS.

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IN a previous paper[1] the senior author has presented results of experiments on the Peltier and Seebeck effects in pure bismuth and alloys of bismuth and tin containing small amounts of tin. The results showed that for these specimens Kelvin's equation, based on the second law of thermodynamics, is true, namely, $P = QT$, where P is the Peltier E.M.F. at the absolute temperature T, and Q is the corresponding thermo-electric power. Whenever these two quantities have been determined for the same metal this relation has been found to hold within the limits of experimental error. A second conclusion was drawn from a comparison of the conductivities of bismuth-tin alloys, as determined by Schulze,[2] and the Peltier and thermo E.M.F.'s, as determined in these experiments. Owing to irregularities in the cross-sections of the specimens used the conductivities of these specimens were not determined at the time. Later rough determinations of these conductivities were carried out by a student in this laboratory, and these seemed to indicate that the conductivities of the specimens were quite different from those determined by Schulze. In consequence, it seemed possible that the second conclusion was untrue, namely, that the thermo-electric power was given by the equation

$$Q = \frac{2R}{e} \log\left(\frac{n_1}{n_2}\right), \tag{1}$$

rather than by the equation

$$Q = \frac{R}{e} \log\left(\frac{n_1}{n_2}\right), \tag{2}$$

where R is the gas constant and is equal to 8.315 joules per degree Centigrade, and e is the Faraday, or the amount of electricity which will deposit from an electrolytic solution a mass in grams of a substance numerically equal to its chemical equivalent, and is equal to 96,500 coulombs, and n_1 and n_2 are the numbers of electrons in unit volume of the two metals used in determining the thermo-electric power.

In order to remove any doubt on this point and also to facilitate experiments upon the Thomson effect, which are considered in another paper,

[1] PHYS. REV., N. S., Vol. VII., pp. 269–277, February, 1916.

[2] Ann. der Phys., 9, pp. 555–589, 1902.

the following experiments were undertaken. Mr. McKay having enlisted in the naval reserves it has fallen to the lot of the senior author, who supervised Mr. McKay's work, to write this paper and also to check Mr. McKay's determinations. The work of preparing the specimens and of making a long series of measurements was done by Mr. McKay. The specimens were made by alloying known weights of Kahlbaum's reagent bismuth and Kahlbaum's purified tin. The metal was fused and thoroughly stirred in an electric furnace and then poured into the mould, care being taken to prevent oxidation of the metal. The mould consisted of two iron slabs one cm. thick. These were machined so as to fit very closely and were held together by nine stout bolts. Suitable grooves in each of the slabs formed a mould giving a ⊓-shaped casting, 19 cm. on each side and having a circular cross-section 0.415 cm. in diameter. Before pouring the metal into it, the mould was heated to a temperature of about 250° C. The mould was then allowed to cool slowly, thus annealing the specimen. Considerable difficulty was experienced in removing the casting from the mould. Satisfactory results were finally obtained by carefully wiping the grooves of the mould with flake graphite before making each casting.

Table I.

Specimen.	Conductivity in Reciprocal Ohms at					
	20° C.	35° C.	50° C.	65° C.	80° C.	95° C.
Pure bismuth No. 1	9,060	8,570	8,080			
" " No. 2	8,890	8,495	8,100	7,705	7,310	6,915
1 per cent. No. 1	3,007	2,955	2,907	2,877	2,860	2,845
" " " No. 2	3,250	3,192	3,144	3,104	3,072	3,054
2 per cent. No. 1	3,334	3,250	3,188	3,134	3,092	3,055
" " " No. 2	2,952	2,882	2,826	2,782	2,746	2,716
3.71 per cent. No. 1	3,310	3,225	3,155	3,095	3,035	2,990
" " " No. 2	3,204	3,115	3,043	2,982	2,933	2,890
6.36 per cent. No. 1	4,460	4,325	4,195	4,068	3,943	3,818
" " " No. 2	4,336	4,208	4,080	3,952	3,824	3,696

For the conductivity determinations the specimens were immersed in a water bath ranging in temperature from near 0° C. to near 100° C. The resistance was measured with a Kelvin bridge. No allowance was made for the conductivity of the water because its conductivity was so very small in comparison with those of the specimens as to make the correction very much less than the probable experimental error. In Table I. the conductivities for a number of different temperatures are given as read from graphs showing all of the individual determinations. The percentage given indicates the percentage of tin by weight in the alloy. It will be observed that there are two specimens of each percentage. This is due to the fact that two specimens were needed for the Thomson effect. It will also be observed that two specimens identically the same in so far as it was possible to make them differ slightly in their conductivities. This is also true of their thermo-electric properties. The conductivities of the pure bismuth and of the alloys containing 6.36 per cent. tin are, within the range of temperatures considered, linear functions of the temperature.

The determinations of the thermo E.M.F. were made in the usual way, the ends of the specimens being connected to copper leads, the one junction being placed in a bath of melting ice and the other in a water bath, the temperature of which ranged from about 15° C. to the boiling-point of water. The E.M.F. was measured by a potentiometer at intervals of about 10° C. The expressions given in Table II. indicate quite accurately the results of these experiments, except in the case of the 3.72 per cent. specimens between 80 and 100° C. In this interval the observed values were slightly more negative than the expression would indicate, apparently showing, when compared to copper, a maximum at about 92° C. For purposes of comparison the thermo-electric powers compared with copper and also with the pure bismuth No. 2, the most electro-positive specimen, are also given in the table. Both of these are computed from the values given in column 2. t is the temperature in Centigrade degrees.

TABLE II.

Specimen.	Thermo E.M.F. Against Copper in Microvolts.	Thermo-electric Power Against Copper in Microvolts per °C.	Thermo-electric Power Against Bismuth No. 2 Microvolts per °C.
Pure bismuth No. 2.......	$40.8t + .25t^2$	$40.8 + .50t$	
" " No. 1.......	$39.5t + .25t^2$	$39.5 + .50t$	-1.3
1 per cent. No. 1.........	$-6.35t + .165t^2$	$-6.35 + .33t$	$-47.15 - .17t$
" " " No. 2.........	$-7.2t + .17t^2$	$-7.2 + .34t$	$-48.0 - .16t$
2 per cent. No. 1.........	$-24.4t + .157t^2$	$-24.4 + .315t$	$-65.2 - .185t$
" " " No. 2.........	$-27.5t + .31t^2$	$-27.5 + .62t$	$-68.3 + .12t$
3.72 per cent. Nos. 1 and 2	$-29.4t + .12t^2$	$-29.4 +..24t$	$-70.2 - .26t$
6.36 " " No. 1.......	$-38.3t + .13t^2$	$-38.3 + .26t$	$-79.1 - .24t$
" " " No. 2.......	$-40.5t + .13t^2$	$-40.5 + .26t$	$-81.3 - .24t$

In Table III. the ratios n_1/n_2 are given, where n_1 is the concentration of the electrons in the specimen mentioned in the left-hand column and n_2 is the concentration in the pure bismuth specimen No. 2. These ratios have been computed in three ways: first, by means of Drude's equation,[1] being (1) given at the beginning of this paper; secondly, by

[1] Ann. der Phys., 1, p. 590, 1900.

J. J. Thomson's equation,[1] being (2) given at the beginning of this paper; and thirdly, from the ratio of the conductivities, this ratio being the same

Table III.

Specimen.	Values of the Ratio n_1/n_2 from		
	Drude's Equation.	Thomson's Equation.	Conductivities.
Pure bismuth No. 1	0.992	0.982	0.998
1 per cent. No. 1	0.7241	0.5243	0.3588
" " " No. 2	0.7224	0.5219	0.3882
2 per cent. No. 1	0.6494	0.4217	0.3932
" " " No. 2	0.6925	0.4796	0.3488
3.72 per cent. No. 1	0.6173	0.3811	0.3895
" " " No. 2	0.6173	0.3811	0.3756
6.36 per cent. No. 1	0.5895	0.3475	0.5176
" " " No. 2	0.5804	0.3369	0.5035

as the ratio of the concentrations if the mean free path of the electrons is the same in both metals. This is assumed to be the case, the assump-

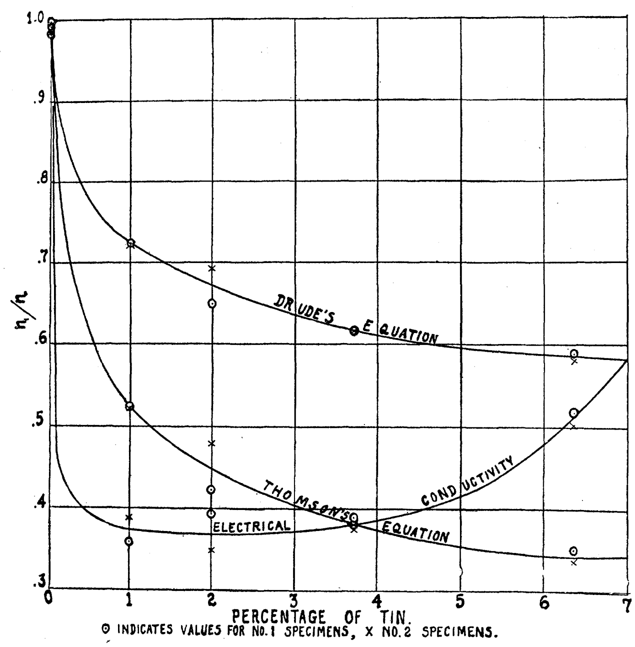

Fig. 1.

tion being discussed at considerable length in the senior author's previous paper. All calculations are for 50° C.

[1] Corpuscular Theory of Matter, p. 74.

It will be observed that for the smaller percentages the figures given in the third and fourth columns agree more closely than do those in the second and fourth columns. Since it is with the smaller percentages that we would expect the assumption of the equality of the lengths of the mean free paths of the electrons to hold most closely, it follows that the ratios derived from the electrical conductivities are in better agreement with those calculated from Thomson's equation than with those calculated from Drude's, although the agreement in neither case is close enough to be considered a justification of the proposed formula.

The data given in Table III. is shown graphically in Fig. 1.

Summary.

The conductivities of pure bismuth and bismuth-tin alloys, containing small amounts of tin, have been measured, and it is found that the addition of a very small quantity of tin increases the resistance of the bismuth very considerably, but with further additions the resistance decreases.

The thermo-electric power of the same specimens has been determined.

A comparison of the two sets of results seems to indicate that Drude's equations for the thermo-electric power and the Peltier E.M.F. are not preferable to Thomson's, but that the reverse is probably true.

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