FURTHER EXPERIMENTS ON BISMUTH THERMOPILES.*

BY

WM. W. COBLENTZ, Ph.D.,

Associate Physicist, U. S. Bureau of Standards.

THE bismuth-silver thermopile appears to be winning a favorable place among the numerous devices employed in measuring radiant energy. The object of the present note is to describe experimental tests illustrating the shortcomings of some of the theoretical deductions relative to the construction of thermopiles.

1. *Relation between External and Internal Resistance.*—The older theories held that the maximum efficiency is attained when the external (the galvanometer) resistance is the same as the (internal) resistance of the thermopile. During recent years, however, Altenkirch¹ came to the conclusion, theoretically, that the external resistance can be two to three times the internal resistance of the pile, without seriously affecting its maximum efficiency. It therefore seemed desirable to subject the question to experimental test. In a previous paper² it was found, when the three units of a large surface thermopile were connected in series, thus producing an internal resistance which was about 6.4 times the external (galvanometer) resistance, that the radiation sensitivity was about two-thirds that of the thermopile having the units joined in parallel and having practically the same resistance as that of the galvanometer.

In the recent experiments the external resistance was greater than the internal resistance. In one outfit consisting of a galvanometer having four coils of 21 ohms resistance, and a thermopile having a resistance of 9.7 ohms, the radiation sensitivity was the same when the coils were in series-parallel (21 ohms) or all in parallel (5.3 ohms). The test was, of course, not very crucial, for it showed simply that when the external resistance was twice as great, or only half as great as the internal resistance,

* Communicated by the author.

¹ Altenkirch, *Phys. Zeitschr.*, 10, p. 560 (1909).

² Coblentz, *Bull. Bur. Standards* 9, p. 7 (1912).

the sensitivity was the same. The crucial test was made with a galvanometer consisting of 26-ohm coils mounted in the soft iron shields previously described.³ This magnetic shield was sufficient to eliminate the ordinary magnetic disturbances and at the same time easily permitted the joining of the coils in various combinations: (1) all in series, (2) all in parallel, (3) two in series-parallel, giving 104, 6.5, and 26 ohms respectively. The thermopile was exposed to a standard of radiation⁴ consisting of a seasoned incandescent lamp calibrated against a black body. Using a thermopile, having a resistance of 13.9 ohms, and an external resistance of 104 ohms, the radiation sensitivity was 31 per cent. less than when the external resistance was 26 ohms,—*i.e.*, the galvanometer resistance was respectively eight and two times that of the thermopile.

The most important test was with a thermopile having a resistance of 6.8 ohms. When the external resistance was four times (*i.e.*, 26 ohms) that of the thermopile the radiation sensitivity was 16.4 to 17 per cent. less than when the external resistance (6.5 ohms) was the same as the internal (thermopile) resistance. In view of the fact that there was a loss of only 16.5 per cent. in efficiency when the external resistance was four times the internal resistance, and in view of the fact that one rarely meets with conditions where the galvanometer resistance is more than twice the resistance of the thermopile, it is evident that this question proves to be of minor importance. Nevertheless, it was important to settle the question, for one of the first specifications of intending purchasers of these instruments is that the resistances of the two instruments must be equal.

2. *The Radiation Sensitivity of a Thermopile.*—The factors which determine the radiation sensitivity of a vacuum thermopile, as enunciated by Johansen,⁵ are as follows: (1) The resistance of the thermopile should be equal to that of the galvanometer; (2) the radii of the two wires of the element should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both; (3) the heat loss by conduction through the wires should be equal to the heat loss by radiation

³ Coblentz, *Bull. Bur. Standards* 9, p. 7 (1912) (see Fig. 17).

⁴ "A Secondary Standard of Radiation," *JOUR. FRANKLIN INSTITUTE*, 176, p. 219 (1913).

⁵ Johansen, *Ann. der Phys.* (4), 33, p. 517 (1910).

from the junctions; (4) the radiation sensitivity is proportional to the square root of the exposed surface.

In previous papers⁶ it was shown experimentally that rules (2) and (4) are only approximately true. In fact, the best diameter of silver wire (0.036 to 0.038 mm.) to be used with a 0.1 bismuth wire was found without considering the theory. In the same manner an iron wire 0.0308 mm. diameter was found better than one 0.0418 mm. in diameter, although theory would have required the thicker wire.

Rule (3) tells us nothing but what must be obtained by experiment, and that must be obtained on a complete thermopile. For example, one would naturally try to use flat bismuth wire to avoid heat conduction. The test, using a single pair of junctions, showed⁷ that the flat wire gave a radiation sensitivity which was about 9 per cent. higher than that of a junction made of round wire. A thermopile was therefore constructed with the greatest care. It embodied the experience and improvements resulting from the construction of 21 thermopiles. It contained 28 elements; had an area of 2 by 14.5 mm. and a resistance of 13.5 ohms. It proved to be the quickest acting of all the instruments yet constructed, but its intrinsic radiation sensitivity (*i.e.*, sensitivity per mm.² of exposed surface) was only 16.4, when all the others, similarly constructed, of round wires had a radiation sensitivity of 25.5 to 26.

The results showed that in smoking the thermopile the flat wires were given a different relation between the emissivity and conductivity than obtained in the round bismuth wires. Johansen's rule (3) was not fulfilled; and nothing but a prolonged experiment sufficed to determine the best mode of construction. The bismuth-silver thermopile is based upon experiment. Its novelty is the completely opaque receiver, while at the same time maintaining a symmetry of the hot and the cold junctions as found in the Rubens and older types of thermopiles.

⁶ Coblenz: *Bull. Bur. Standards* 9, p. 7 (1912). *JOURNAL FRANKLIN INSTITUTE*, 175, p. 497 (1913). *Physikalische Zeitschr.*, xiv, 683 (1913). *Jour. Wash. Acad. Sci.*, 3, p. 357 (1913). These experiments were made on thermopiles in air. There is a distinct field of investigations requiring thermopiles in air.

⁷ Coblenz: *Phys. Zeitschr.*, xiv, 683 (1913). *Jour. Wash. Accd. Sci.*, 3, p. 357 (1913).

In some forms of thermopiles now being put on the market the cold junctions are attached to the metal supporters. This introduces a dissymmetry between the hot and cold junctions, and hence a likelihood of "drift" of the galvanometer needles. For the incident radiation warms the surrounding air, and the cold junctions, because of their greater heat capacity, cannot quickly take the temperature of the surroundings.

By making the small receivers twice as long and attaching two junctions to each receiver, less shellac is required for insulation between the hot junctions, and the heat capacity, the emissivity, and the resistance are reduced. A thermopile built on this principle, consisting of nine pairs of junctions joined in series-parallel, had a resistance of 2.2 ohms. If the 18 elements had been joined in series the resistance would have been four times as great. In this thermopile the receivers were 2 by 2.1 mm., making a completely opaque curtain 2 by 18.5 mm. in area. The device is more sensitive and quicker acting than the old style, and it was entirely free from drift.

The receivers are made of platinum, which remains bright on the rear, unprotected side, thus keeping a low emissivity. Silver receivers might be better when new, but eventually the rear (unprotected) side would become black, thus increasing the emissivity. The use of thin metallic receivers permits a modification of the device to suit the individual problem. For example, in a physiological problem involving the question of the heat produced in a stimulated nerve the receiver is built in the form of a long, U-shaped trough, 21.5 mm. in length, within and along the axis of which is suspended the sample under investigation. This thermopile receives heat by radiation and by conduction from the material placed within the U-shaped receiver. The sensitivity (approximate value) was tested by placing a silk-covered manganin wire (0.05 mm. diameter, resistance 4.5 ohms) within the receiver, and passing an electric current through it. Using a galvanometer sensitivity of 5×10^{-10} ampère, a deflection of 1 mm. = 4.3×10^{-8} watt, or 1×10^{-8} calorie was shown.

It is desirable to emphasize the importance of examining the electromotive force of the bismuth wire. Of the eight samples tested (diameters 0.06, 0.08, 0.1, and 0.15 mm.), the thermoelectric power, against silver, varied from 75 to 82 microvolts. This seems to depend upon the purity of the material, as indicated

by the purchases at different times. The material received in one order of 0.08 and 0.1 mm. bismuth wire gave 76 microvolts, while another order consisted of material giving 75 and 82 microvolts respectively.

The electromotive forces of various thermopiles, exposed to a standard of radiation, was measured with an ordinary potentiometer. The actual voltages developed varied from 6 to 20 microvolts (depending, of course, upon the number of thermojunctions, and especially upon the area exposed), which was equivalent to 0.20 to 0.25 microvolt per microwatt. One thermopile gave 0.35 microvolt per microwatt. The efficiency per single junction, in the thermopiles examined, varied from 0.011 to 0.014 microvolt per microwatt of radiant energy. Since the thermoelectric power is about 78 microvolts, the results show that 1 microwatt produces a rise in temperature of about $15^{\circ} \times 10^{-5}$ C. above the surrounding air. This seems the most logical way to rate the efficiency of a thermopile.

In most of the thermopiles there was but little gain by placing more than one thermojunction per 0.8 mm. length of the complete receiver, and ordinarily it would be sufficient to place them at a distance of 1.2 mm. length. This should be sufficient to give a correct integration of the incident radiation if it should not be uniformly distributed.

Recent investigations⁸ show that an alloy of Bi + 9 per cent. Sb gives a higher electromotive force than pure bismuth; but this alloy is too brittle for thermopiles. The best combination which gives fine annealed threads, by spattering,⁹ is Bi + 4 per cent. antimony. The electromotive force of the material must be tested, however, for some samples give a lower electromotive force than the best wire of pure bismuth.

An alloy of Bi + 5 to 6 per cent. tin gives 44 to 45 microvolts. When used with the best bismuth wire the thermal element

⁸ Haken: *Ann. der Phys.* (4), 32, p. 291 (1910).

Gelhoff and Newmeier: *Verh. Phys. Gesell.*, 15, p. 876 (1913).

⁹ Coblenz: *Bull. Bur. Standards* 7, p. 248 (1910). This method, which seemed too ridiculous for description at that time, is one of the chief contributions to the improvement of thermopiles. By dropping the molten metal from a height, upon an inclined glass plate, the metal is drawn out into thin, well-annealed threads. Pfund (*Phys. Rev.*, 34, p. 228, 1912) goes a step further, and hurls the molten metal against the glass plate. This produces longer threads, of great uniformity.

gives an electromotive force of 126 to 128 microvolts. An element consisting of pure bismuth wire and an alloy of Sb, Cd, Bi gave 138 to 140 microvolts per degree; but the alloy is too brittle for an ordinary thermopile. The most promising thermopile appears to be one having elements of pure bismuth and an alloy of Bi + 6 per cent. tin, joined in series-parallel, as already described.

In conclusion it may be added that in the discussion of theory *versus* experiment it is not intended to detract from the theoretical contribution to the subject. On the other hand, it is but fair to emphasize the contributions which had to be worked out experimentally. These experiments relate to the most crucial points in thermopile construction, especially the question of heat conduction and emissivity, upon which theory could be of little assistance.

WASHINGTON, D. C., October 25, 1913.

Natural Gaseous Mixtures Rich in Helium. C. MOUREU and A. LEPAPE. (*Compt. Rend.*, clv, 197.)—The following mineral springs evolve gas containing a large percentage of helium. The natural gas from the springs at Sautenay contains from 8.4 to 10.1 per cent. of helium, that from springs at Maizières contains 5.9 per cent.; from springs at Grisy, 2.18 per cent.; from Bourbon Lancy, 1.84 per cent.; from Nérès, 0.97 per cent.; and from La Bourboule, only 0.1 per cent. The quantities are too large to be considered as nascent helium evolved immediately it is produced; and it is more probable that the immediate source is dissolved helium, evolved by the disintegration of minerals in which it has been absorbed. These sources are grouped in the neighborhood of Moulins, Dijon, and Vesoul.

Pressure-Balanced Piston Rings. ANON. (*Eng.*, cxv, 521.)—This paper describes piston rings by Allen and Simmons, Ltd., which are designed to decrease the friction of piston rings and, consequently, the lost power. The fundamental idea is to balance the outward radial pressure of steam behind the rings by giving them a suitable cross section. It is shown by calculation that, whereas the frictional losses caused by Ramsbottom rings might be 4.8 per cent., the loss with the Allen rings is only 0.173 per cent. The same idea is applied to piston valves, air-pump buckets, and gland packing. It is also shown that it is possible, by the use of Allen rings, to employ a very simple form of piston, which is cheaper to construct and is more efficient thermally than the ordinary type.