

## A BISMUTH-SILVER THERMOPILE.

BY

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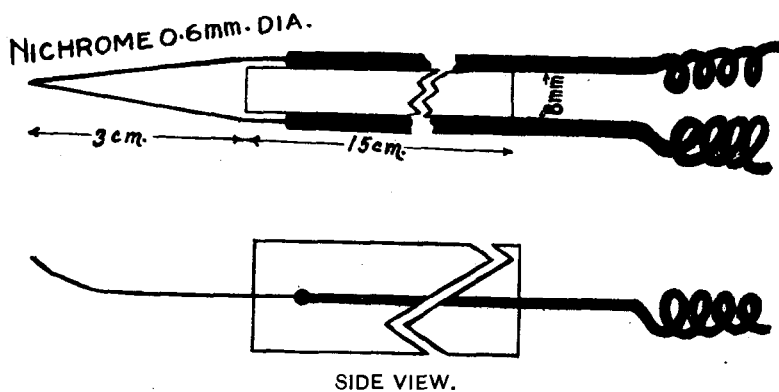
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BEING able to purchase fine bismuth wire (from Hartmann and Braun), an attempt was made to use a pile constructed of bismuth iron, soldered with Wood's alloy. The iron was first tinned so as to make good contact. It was found that the resistance of a single junction arose from 1.5 ohms to 3 ohms, and some to 90,000 ohms, in a few days, and the whole was therefore discarded. In view of the fact that iron rusts easily, that the Bi-Fe junctions were weak, and that the thermoelectric power of Fe is about five times that of Ag, while its resistance is from six to ten times that of Ag, there is no particular advantage in using iron instead of silver. The welding of bismuth to silver makes a very strong junction. It was found that the direct welding of Bi to Ag was somewhat difficult. A small bead of tin, about 0.1 mm. in diameter, was therefore melted to the silver wire (Ag = 0.051 mm. diameter) by means of a small heater of nichrome wire filed thin at the point, shown in Fig. 1. The end of the bismuth wire (Bi = 0.1 mm. diameter) was then brought into contact with this bead of tin (probably an alloy of Sn and Ag), which was then melted with the nichrome heater. Contrary to some of the prevailing notions, such a heater is better adapted to delicate work of this type than is a well-tinned soldering copper; for the surface tension of the molten material on the hotter surface of an ordinary soldering instrument is sufficient to tear fine bolometer strips. The bismuth wire is too brittle to permit flattening the junction, so that a small rectangle of pure tin  $1.4 \times 0.6 \times 0.025$  mm. was then placed under the Bi-Ag junction and fused thereto with a quick touch of the nichrome heater. It is somewhat easier to flatten the tin bead attached to the silver wire and then fuse the bismuth to this flat disk (see lower part of Fig. 2), but in this case it is not so easy to produce a receiving surface which completely fills the thermopile slit. Sheet silver, 0.02 mm. in thickness, is better than tin for a receiving surface,

because it does not melt in attaching it to the junction. In this case the tinned silver wire may be attached to the sheet of silver and then the bismuth wire is melted thereto.

There are many points in favor of the use of silver instead of copper in this type of thermopile. It is easily annealed and the brown oxide is easily removed by heating the wire on a sheet of metal. Thus cleaned, the bead of tin is easily attached without any soldering acid. A bit of rosin is useful but not necessary in attaching the bismuth wire. The low resistance (0.08 ohm

FIG. 1.  
TOP VIEW.

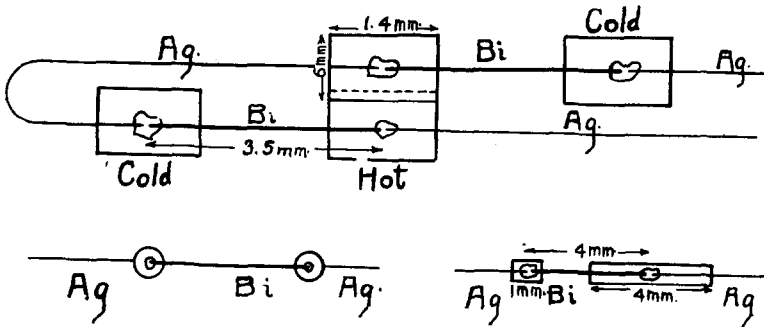


SIDE VIEW.  
Nichrome welding instrument.

per metre), and especially the pliability of silver, are also important items, which one appreciates after working with iron and constantan wires. The bismuth wire is not so pliable, but it is short, and since it is subject to very little usage in mounting it is not easily broken. Before mounting them the various junctions were given a thin coat of shellac on the rear side, for insulation, and painted with a mixture of lampblack and chemically precipitated platinum black in turpentine on the front surface. The junctions were then mounted, slightly overlapping upon a glass plate, with Le Page's glue, and the ends of the silver wires were soldered together as shown in Fig. 2. The glass plate was then mounted on an ivory frame and the loose ends of the silver wires were attached thereto. The glass plate was then removed by soaking in water, thus leaving a uniform, solid, well-insulated

receiver as shown in Fig 3. Subsequently all these junctions were separated and the resistance of the pile was then found the same as when the junctions were in contact, showing that the insulation was perfect. The silver wires were then given a thin coating of shellac; but this was not necessary. The length of the receiving surface of this pile, consisting of 20 junctions, is 12 mm. The great width, 1.3 to 1.4 mm., of this particular pile was chosen for a special research in which high sensitivity was required. The rectangles or disks of tin may be much smaller, as in the new form of Rubens thermopile.

FIG. 2.



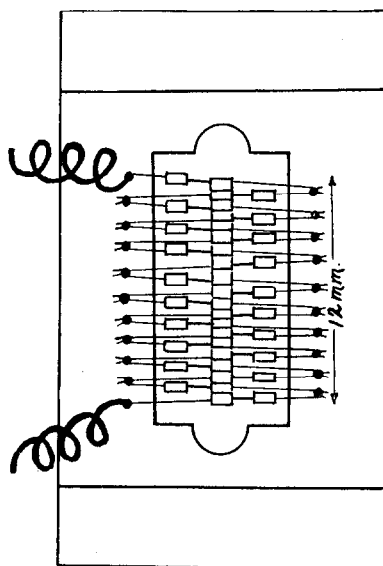
The thermoelectric power of this bismuth-silver thermocouple is 89 microvolts per degree, as compared with an iron-constantan couple which is 51 to 53 microvolts per degree. The *temperature* sensitivity of Bi-Ag is therefore about 74 per cent. greater than an iron constantan thermopile. Whether the *radiation* sensitivity is increased in like proportion will depend upon the selection of the proper diameters of wires, as will be found presently in this thermopile, in which the radiation sensitivity is two to three times that of the iron-constantan pile. The new form of iron-constantan thermopile of fine wires has a resistance of about 9 ohms. The present example of bismuth-silver has a resistance of 9.3 ohms.

The radiation sensitivity of this bismuth-silver pile and of an iron-constantan pile was tested, side by side, by joining the two instruments through a mercury switch to a galvanometer of 5.3 ohms resistance and  $i = 4.6 \times 10^{-10}$  ampere. A standard sperm candle placed at a distance of 2.4 m. caused a deflection

of 10.2 cm., or 59 to 60 cm. for a candle and scale at 1 metre when the bismuth-silver pile was exposed. With a galvanometer sensitivity three times as large, as it is ordinarily used, the total deflection would have been about 180 cm.

The Rubens thermopile, of wires about 0.15 mm. in diameter and having a resistance of 4.7 ohms, when similarly exposed, caused a deflection of 3.8 to 4.0 cm, or about 23 cm. for a candle

FIG. 3.



Bi-Ag linear thermopile.

and scale at 1 m. The receiving surfaces of this pile were about 1.5 mm. diameter and about 0.2 mm. thick. The disks overlapped so that the 20 junctions occupied a space 20 mm. long. The actual area exposed was therefore greater than in the first bismuth-silver pile, which had a receiving surface of about 16 mm.<sup>2</sup> This comparison shows that the radiation sensitivity of this bismuth-silver pile is about 2.6 as sensitive as the ordinary Rubens silver pile. If we consider that in spectroradiometry we are interested in the length (height) of the spectrum which can be utilized we should have made the length of the Bi-Ag pile 20 mm. by adding more couples. The radiation sensitivity of the

Bi-Ag pile would therefore be increased by  $20 \div 12$ , or a total deflection of about 100 cm. instead of 60 cm. as observed. It is therefore safe to say that, comparing equal lengths of receiving surface utilized on a spectral line, the radiation sensitivity of this type of Bi-Ag pile is four times that of the old type of low resistance, iron-constantan pile. If we compare the bismuth-silver pile with the fine wire type of iron-constantan pile, which has a resistance of 8.9 to 9.3 ohms and has a radiation sensitivity of 1.4 times that of the old Rubens type of pile, it is a fair estimate to say that this pile has a radiation sensitivity three times as great as the new type of iron-constantan pile.

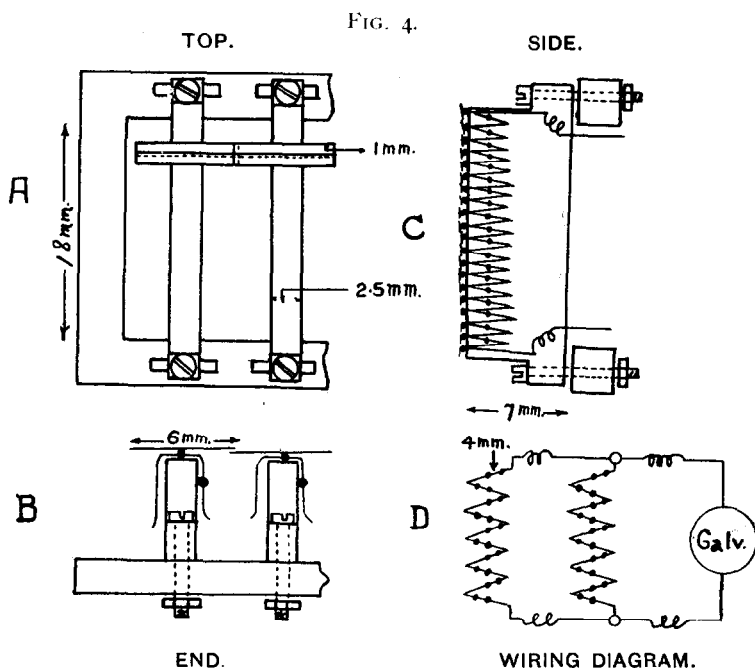
One important point usually not considered is the heat capacity, and hence the speed of attaining temperature equilibrium in these instruments. In the present radiation sensitivity tests the time of single swing of the galvanometer was 2 seconds. When joined with the bismuth-silver pile the half period was lengthened to about 3.8 seconds, which is practically the same as for the new type of fine wire iron-constantan pile. This is not an excessively long period, and the deflection returns abruptly to its zero position. But in the old type (heavy wire) of iron-constantan pile, tested alongside of the bismuth-silver pile, the time of single swing of the galvanometer was increased from 2 seconds to about 6.5 seconds, and there was a tendency to lag, especially when measuring intense radiation, so that it does not compare favorably with the Bi-Ag pile. This pile of bismuth-silver was designed for special work using a large receiving surface in air, where very thin metal is easily affected by air currents. The hot and the cold junctions are sufficiently alike in size and emissivity so that there is no permanent temperature difference and consequent drift in the instrument. The junctions are easily made and mounted, and they are equally easy to repair if broken. The iron-constantan pile of fine wire is difficult to handle and difficult to repair if broken.

By using an alloy of platinum-iridium instead of silver the thermoelectric power would be increased, but owing to the increased resistance it remains to be determined whether a higher radiation sensitivity would be obtained.

The present instrument is not intended for rapid work, but for an exact and undisturbed register of observations with the instrument in air. While the time to attain temperature

equilibrium is somewhat longer (less than 4 seconds) than was hoped for, it is not sufficient to cause annoyance. By reducing the heat capacity, by using thinner wires, temperature equilibrium should be attained in less than 3 seconds.

The success attained with the linear pile led to the construction of a thermopile having a large receiving surface built up of single units, each of which contains 20 or more thermoele-



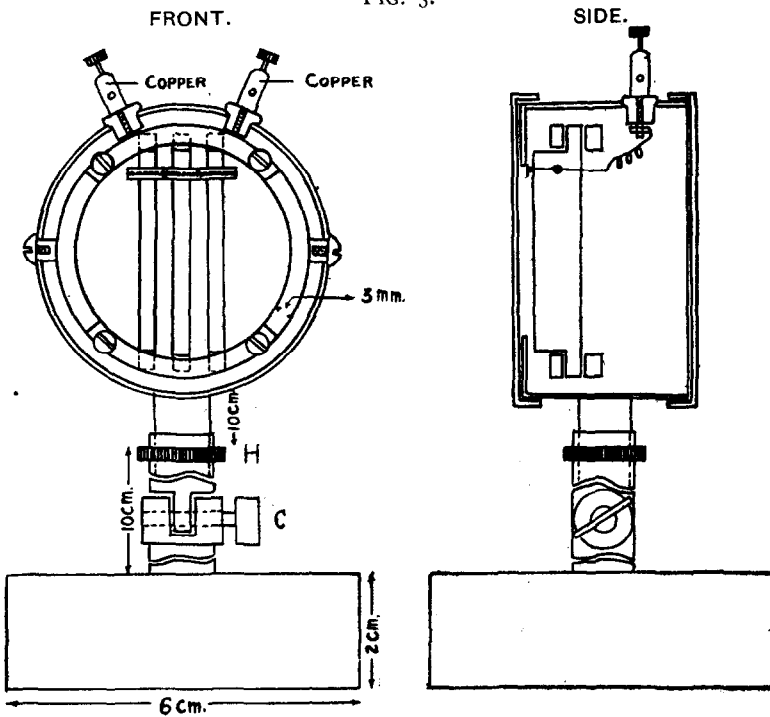
Surface thermopile of bismuth-silver.

ments, mounted upon an ivory support as shown in Fig. 4, C. In the preliminary tests as to the most desirable widths of strip to be used, thermoelements were built with receivers of the same width, 0.6 mm., and of different lengths, as shown in the lower part of Fig. 2. In all cases the silver wire used was 0.0513 mm. in diameter. The bismuth wires (4 to 5 mm. long) examined were 0.06 and 0.15 mm. in diameter. The two receiving surfaces were blackened, and they were exposed alternately to radiation. The elements to be tested were enclosed in order to avoid air currents. Using bismuth wire 0.15 mm. in

diameter, the deflection for a receiver 4 mm. long was not quite twice that of a receiver 1 mm. long. For both receivers the deflection did not attain a maximum abruptly, and there was a serious "creeping" requiring some 15 seconds for the galvanometer to come to rest.

Using bismuth wire 0.06 mm. in diameter the galvanom-

FIG. 5.



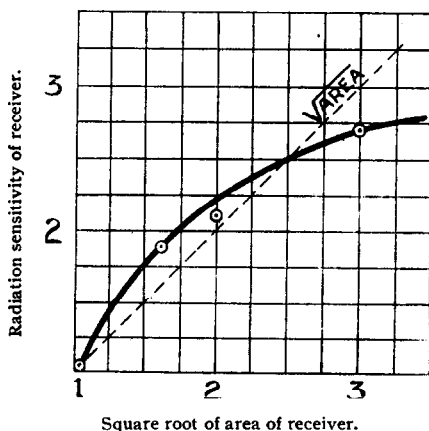
Holder for thermopile.

eter deflection for a receiver 4 mm. long was 2.1 times as large as that of the receiver 1 mm. long. On reducing the length of the 4 mm. receiver to about 2.6 mm. the sensitivity was 1.9 times as great as the receiver 1 mm. in length. A receiver 9 mm. long was 2.7 times as sensitive as that of a receiver 1 mm. in length. As shown in Fig. 6, the sensitivity varies roughly as the square root of the receiving surface, which is the law of the surface bolometer. As a matter of fact, there is an optimum length of the order of 2 mm.; but this exact value was not

determined. Obviously two receiving surfaces 4 mm. wide are better than a single one 9 mm. wide in the ratio of 4.2 to 2.7. In fact, the sensitivity would be still greater than this by placing two units (4 mm. wide) in parallel; for the internal resistance is reduced to one-half the former value. Units which are built up with receiving surfaces 4 to 6 mm. wide give ample working space in mounting, so that there is a distinct gain in using such narrow widths.

No difference could be detected in the sensitivity of the front and rear surfaces of these junctions, showing that attach-

FIG. 6.



ing the junction at the centre of the receiver is not detrimental.

The size of the receiver made no appreciable difference in the time of attaining a temperature equilibrium. In designing the surface thermopile it was therefore deemed permissible to omit the receiving surfaces from the "cold," unexposed junctions. For fine wire the deflection attained its maximum abruptly in 3 to 4 seconds.

In a vacuum of 0.15 mm. pressure of mercury the thermoel-  
ement of bismuth wire 0.06 mm. in diameter was 2.03 times as sensitive as in air. It is therefore a distinct advantage to place the pile in an evacuated enclosure.

Using the same size receivers, the radiation sensitivity of the thermoelement of bismuth wire 0.15 mm. in diameter was twice as sensitive as the element of bismuth wire 0.06 mm. in



diameter. But the serious lag in attaining temperature equilibrium in a thermopile of bismuth wire 0.15 mm. in diameter is objectionable, so that it is to be recommended only where a very high sensitivity is required and where the radiation is very weak.

In the surface thermopile it was therefore decided to use bismuth wire 0.1 mm. in diameter and silver wire 0.05 mm., which increases the radiation sensitivity closely to that of the element with bismuth wire 0.15 mm. in diameter and leaves the time of attaining temperature equilibrium about the same as that of the element having bismuth wires 0.06 mm. in diameter. The various elements, joined in parallel as shown in Fig. 4, D, reduce the resistance and increase the sensitivity. By having the units of closely the same resistance there will be but little shunting of the current generated.

In making the units, the individual elements are mounted in a row upon a glass plate, as previously described for the linear pile. The ivory support is then placed over the central line of receivers and the end wires are bent back against the side of this support (shown in Fig. 4, B, C) and attached thereto with boiled shellac or "Khotinsky" cement. The silver wires are then joined as shown in Fig. 4, C. The mounting for these ivory supports (Fig. 4, A) may be of brass and, for convenience in construction, may be circular as shown in Fig. 5. The slight adjustment of the ivory supports necessary in placing them upon this mounting is accomplished by means of slots and bolts as shown in Fig. 4 A, or by means of clamps as shown in Fig. 5.

In Fig. 5 is shown a surface pile made of three units, each consisting of 20 elements. The individual receivers are of tin  $6 \times 1 \times 0.03$  mm., and the total area is about  $17 \times 17$  mm. Obviously the sensitivity to be attained depends upon the number of units, and this depends upon the patience one has in constructing such instruments.

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**The Rôle of Gelatine in the "Chemical" Development Process.** A. P. H. TRIVELLI. (*Chem. Zentr.*, i, 958.)—The presence of gelatine increases the quantity of silver bromide that will be reduced by a definite quantity of developers, and retards the direct reduction of the fixed silver bromide, which gives rise to the developing film.