83. *Residual Thermoelectricity of Mercury Filament.*

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(Rec. June 5, 1928. Comm. by T. TERADA, M.I.A., June 12, 1928.)

The residual thermoelectricity, obtained by heating a small portion of thin metallic wires such as nickel, had been previously investigated by Terada and Tsutsui¹⁾, and it was found that the variation of emf. along the wire shows some correlation with the very slight variation in the sectional diameter of the wire, but this latter variation does not seem to be the direct cause of such thermoelectric phenomena. Moreover, a slight coating and polishing on its surface are found to have some astonishing effects on the character of the thermoelectricity of this kind.

The present experiments were begun with an intention of investigating the effects proper of the geometrical form of the cross section of wire on one hand and those of the thin surface layer on the other. To avoid so-called internal strain of the conductor, Hg was employed, for which C. Benedicks had already declared the existence of "Benedicks Effect" with the aid of his "Drosselkreuz" method²⁾.

Hg was poured into a capillary tube of ordinary soda glass, with an inner diameter of about 0.4 mm. and 50 cm. long, of which a small portion was heated symmetrically with a small furnace specially devised for this purpose. To prevent amalgamation, iron electrodes were dipped into Hg and connected with copper wire to a galvanometer with a sensitivity of 10^{-7} volt per scale division. Junctions of metals of different kinds were kept at constant temperature by wrapping thickly with cotton wool, which was found to be superior to streaming water for the present purpose. At first, readings were taken at every 1 cm. of the position of the heater along Hg column. Emf., such as previously observed in the case of metallic wire, were irregular and varied from one experiment to another. But, in all these experiments the amount of fluctuations of emf. along a Hg capillary column seemed to diminish gradually as the experiments were repeated with the same Hg column. It was suspected that such an emf. may be due to some agencies depending on the condition of

1) Sci. Pap. Inst. Phys. Chem. Res., **7**, No. 122 (1927), 201-235. Proc. Imp. Acad., **3** (1927), 507.

2) Ann. d. Phys., **62** (1920), 185.

contact between Hg and the glass wall. To test this idea, a part of the interior of the capillary was coated with a thin layer of bakelite, but no definite emf. could be observed by heating the junction of the coated and uncoated parts. Next, a capillary tube with an abrupt change of cross section was made, by inserting a short thinner tube about 10 cm. long into the main tube, and similar measurements were then made. It was found that Hg contained within the thinner portion behaves as a quite different material compared with the remaining portion, and a sensible emf.¹⁾ may be easily observed at the junction of the thinner and thicker. In this case also, as described before, the amounts of fluctuations gradually diminished from one experiment to the next. After the fluctuation has thus diminished to a very small amount, the Hg capillary was left alone without any treatment for about a week, and then similar experiments were repeated. It was observed that the emf. has recovered to the previous order of magnitude, which diminished again gradually as before.

After giving a disturbance to the liquid column by moving Hg to and fro along the tube, the first experiment showed a rather great fluctuation of emf. along the capillary, but the second, third etc. generally gave rather flat ones, especially along the part with the thinner tube.

For the verification of the existence of some effects of thermal treatment in such a liquid Hg column, the effects of heating and cooling at the thinner tube were investigated. For this purpose, the following method was employed. The mean value of the first few experiments, which may be regarded to be free from any sensible heat treatment, was taken for the normal, and the difference between emf. of the heated or cooled and the normal cases was obtained respectively and the results were compared with each other. Distinctly opposite characters were observed especially at the portion with the inner tube.

As has been previously shown, such a kind of thermoelectricity can easily be affected by a slight treatment, so that it is very difficult to obtain same results even with the same capillary when the readings are taken at every 1 cm., for the total time of heating at a point is rather long. Therefore, avoiding such a procedure, the readings were taken at every 5 cm. In this case, more reproducible emf.-position curves could be obtained. The variation of emf. thus obtained at the two ends of the thinner capillary tube seems, however, to be deter-

1) Difference between the maximum and minimum of emf. is about 1.5×10^{-7} volt.

mined by a temporary condition of contact between Hg and glass, and by no means by the geometrical form of the cross section. Therefore, with the same capillary we obtain sometimes quite different emf. when Hg is slightly disturbed, not to speak of different kinds of glass. The mean value of a great number of readings obtained with varied conditions shows no sensible systematic variation of emf. at the both ends of the thinner tube, that is, there exists *no purely geometrical effect in this kind of thermoelectricity*.

When a capillary tube of hard glass was inserted into an external tube of ordinary soda glass, the mean value of such readings shows opposite signs of emf. at the both ends of inner tube systematically, though of small amount.

The direction of motion of Hg in developing the fresh effect seems to have some slight effect, though no definite result could be obtained at the accuracy of the present experiments.

Throughout these experiments, there was observed a peculiar temporary emf. which could not be passed unnoticed, that is, when a heater was applied to a point, a sudden and rather great emf. generally about ten times and sometimes hundred times greater than the steady emf. above described, was produced for short time. Again, when Hg was moved and thence probably a fresh surface of contact between Hg and glass was developed, this temporary emf. became great and then diminished by and by. No such emf. has been observed outside of the part with the inner tube. The sign of emf. is sometimes positive and sometimes negative, which seems to be independent of the direction of the inner tube relative to the outer, that of motion of the heater or of Hg. But there is no change of sign of emf. throughout one set of experiments. These facts seem to suggest that when Hg is freshly poured into a capillary tube the contact layer is subjected to a state of "strain," and a temporary emf. is produced when it is released and settles to more stable state by heating.

The present experiments are, of course, insufficient for allowing us any definite conclusion, but the following may at least be stated:

(1) Above observed emf. is not due to any internal structure as in the case of metallic wires.

(2) Purely geometrical form of cross section has no thermoelectric effect in the case of Hg, at the accuracy of the present experiments.

(3) Hg contained in a thinner tube which is inserted in a larger tube behaves as a different material.

(4) The seat of emf. is of unstable nature, especially at the portion of the thinner diameter and at the both ends of it, and the thinner the diameter, the more unstable it is.

Therefore, taken together with the results of recent investigation of E. Hatschek on rigidity of colloidal solutions¹⁾, with some sorts of capillary phenomena such as cataphoresis and also with the previous works²⁾ made in this laboratory, these emf. may probably be attributed to some temporary condition of the contact layer between Hg and glass. Though it is not yet clear whether this is due to properties of glass or of gas adsorbed on the glass surface, it may at any rate be admitted that such a thin layer may play rather important part in such cases of residual thermoelectric phenomena.

Further experiments are in progress.

1) Nature, **119** (1927), 857.

2) loc. cit.