Citation:

Haga, H. & Zernike, F., On thermoelectric currents in mercury, in:
KNAW, Proceedings, 21 II, 1919, Amsterdam, 1919, pp. 1262-1268

Physics. — *"On thermoelectric currents in mercury"* By Prof. H. HAGA and Dr. F. ZERNIKE.

(Communicated in the meeting of March 29, 1919).

In an extensive paper "Ein fur Thermo-electrizitat und metallische Warmeleitung fundamentaler Effect", [1]) C. BENEDICKS endeavours to show the existence of a thermoelectric force in a homogeneous conductor, when at both sides of a heated part the temperature falls off at a different rate, i e. the temperature gradient is different. [2]) He makes due allowance for the possibility of the thermo-electric force which appears under these circumstances in solid conductors being due to changes of structure, which would make the contiguous parts of the conductor behave as different substances. Therefore he considers the proof of the reality of the force mentioned to depend upon the success of experiments with a liquid conductor. To this end he used a glass tube filled with mercury, which had been drawn down at one point, and heated the wider part next to it, thus bringing about a high temperature with slow decrease in the wide part, and steep gradient at the constriction. He did not obtain reliable results from these experiments, which he supposed to be caused by the conduction of heat through the glass. This would heat the mercury in the narrow part and thus prevent the temperature from falling off with sufficient steepness. Against the well-known experiments of MAGNUS, who could not detect any current in bringing into contact mercury conductors of different temperature, and who worked also with unequal temperature gradients, BENEDICKS advances the low sensitiveness of MAGNUS's pointer-galvanometer compared with the mirror galvanometers of the present time.

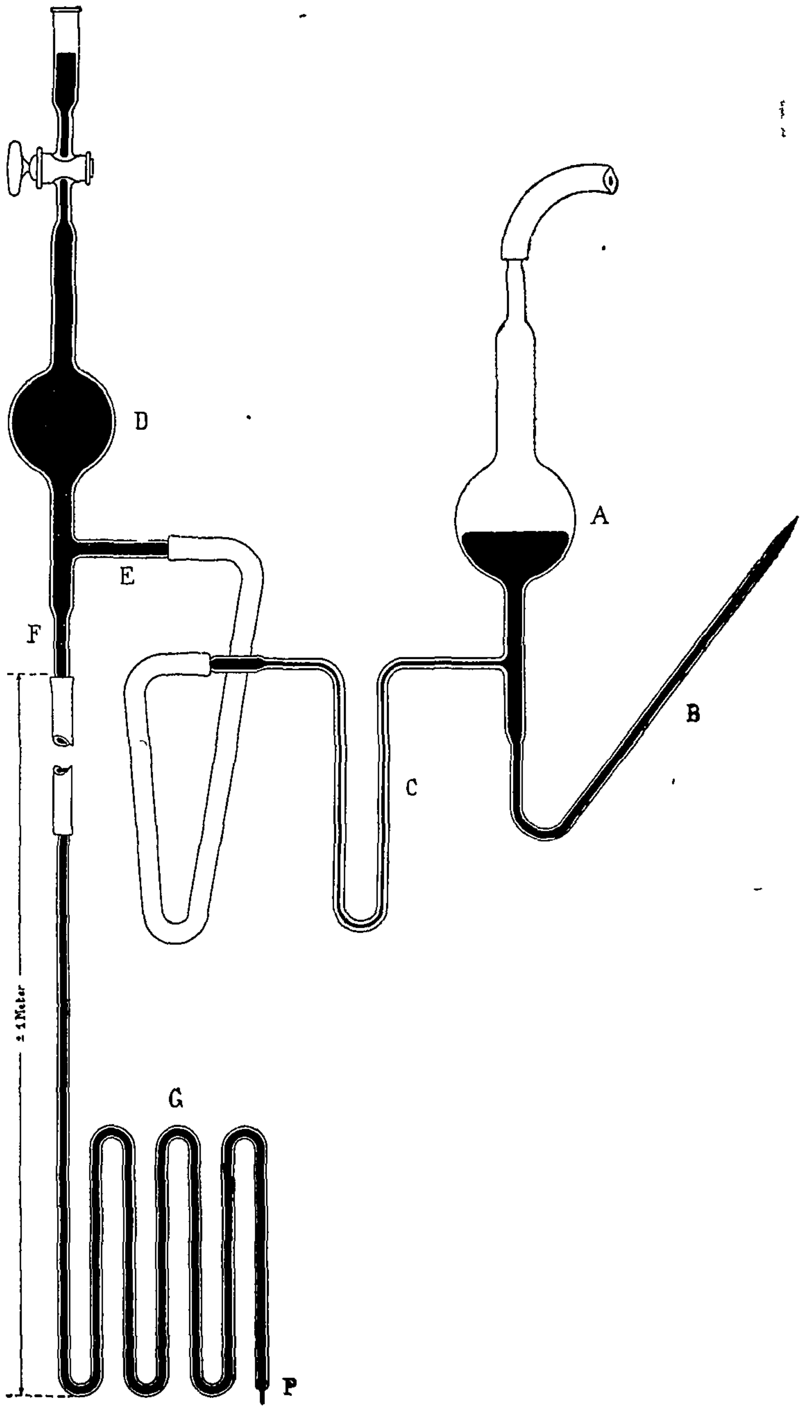
We have devised an experimental method by which, while using mercury, all the conditions of BENEDICKS for a sensitive test [3]) would be met, thus enabling us to get a conclusive decision as to the reality of the new effect. This method consists in the use of two mercury jets joined to a sensitive galvanometer, one of them

[1]) Ann. der Physik. **55**, p. 1—80, p. 103—150. 1918.

[2]) Pogg Ann. **23**, p. 497, 1851. MAGNUS here tried to disprove the production of thermo-electric currents under these circumstances.

[3]) l. c. p. 118.

being heated. The influence of the wall, feared by BENEDICKS, is thus completely eliminated, the surface of contact can be made very small and in this surface the mercury is continuously renewed, thus making the temperature gradient very large and stationary.



The accompanying figure shows the arrangement used. To a glass bulb *A* is attached a tube *B*, the end of which has been

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reduced to a small aperture in the blow-flame. C is a capillary joined to half a metre of rubber tubing, which leads to E. D, E, F form together a second glass part; the lower end of F is joined through another half metre of rubber tubing to G, which is bent three times up and down. At P a platinum wire has been sealed into the glass tube.

Half of bulb A and all the rest of the glass apparatus was filled with mercury distilled in a vacuum. A stout rubber pressure tube was slid over the narrowed top of A and joined at the other end to a reservoir in which air had been brought to a pressure of 2 to 3 atmospheres. The arrangement described served the double purpose of preventing heat being carried by conduction from the heated tube B to the platinum wire P, and also procuring an easy way for refilling bulb A with mercury.

For each mercury jet a similar apparatus had been prepared. The two parts G were tied together and placed in a vessel with water. ($48 \times 24 \times 20$ cm.). To the platinum wires P were soldered the ends of flexible wires covered with rubber and silk, leading to the galvanometer, the junctions and the bare platinum and copper ends being thickly coated with shellac. Two metres of the leads were immersed in the water, thus preventing any conduction of heat either through the mercury or through the copper, and securing perfect equality of temperature of the two mercury-platinum-copper junctions. The resistance of the connecting wires, the tubes with mercury and the mercury jets was 1.5 ohms. The galvanometer used was one of the THOMSON-type, made by CARPENTIER, in which the original astatic system had been replaced by a system according to DU BOIS-RUBENS, made by SIEMENS and HALSKE, suspended by a quartz fibre of 7 μ. The coils had a resistance of 2.7 ohms; the scale-distance was 2.8 metres; the magnifying power of the reading telescope was 33 times.

By adjusting the directing magnet the sensitiveness was raised to a deflection of 1 mm for 5.8×10^{-9} ampère; the total resistance being 4.2 ohms, 1 microvolt produced a deflection of 41 mm. With this sensitiveness, however, we could not make any measurements till after the cessation of the tramway traffic, but then we could trust the reading to within 0.1 mm, unless unusually large fluctuations of the magnetic declination occurred.

One of the apparatus ABC was attached to a solid stand permitting slow displacements in three perpendicular directions.

In order to collect the mercury the nozzles were placed in a short vertical glass tube of 4 cm. diameter, two vertical slots allowing the tubes B to enter. The top of this tube was covered by a wooden ring with a glass window, through which the jets could be observed with the aid of a binocular microscope magnifying 15 times. The jets hit the glass window and the mercury dropped in a beaker placed underneath.

With suitable nozzles the first centimetres of the mercury jets appeared like highly polished metal wires, their diameters being capable of exact measurement on a divided scale in the eyepiece of the microscope.

In the experiments to be mentioned these diameters were 0.10 and 0.13 mm. Farther away from the orifices the surface of the jets was dull, an indication that they had broken up into droplets.

If the adjustable jet was slowly made to approach the other one, the surfaces came into contact, causing the jets to deviate from their original directions, which were perpendicular to each other. A slight displacement wholly changed the aspect: the jets united to a thin membrane, which resolved into droplets after a short distance. With central impact this membrane was perpendicular to the plane of the jets.

The upper part of tube B was surrounded over a length of 16 cm. by a close-fitting copper tube which could be heated by putting a gasburner under it. In this way the flowing mercury could reach a very high temperature. This was evidenced when once the pressure was released immediately after removing the flame, the glass tube being shattered by the sudden abundant development of vapour from the superheated liquid. An exact determination of the temperature seemed superfluous as the experiments were of a tentative character, so we simply estimated it from the aspect of the vapours rising from the jets.

Many series of observations were made on different days, which agreed perfectly with each other. The following table gives one of these as an example. The numbers in the second and third columns are scale readings in mm.

From $1^h\,27^m$ to $1^h\,31^m$ the jets were not heated, and readings were taken alternately with the jets not colliding and colliding centrally. The deflection is caused by spurious thermoforces in the circuit.

After that the gasflame was put under the copper tube, which causing the mercury jet to rise gradually in temperature; the deflections increased at the same time. After the removal of the flame the deflections decreased, resuming the original value, as soon as the mercury had reached room-temperature. By heating the other tube

Time 6 March 1919.	Scale readings.		Deflection.
	Jets free.	Jets in contact.	
$1^h\ 27^m$	154.2		
		161.9	+ 7.9
	153.8		
		161.9	+ 8.0
	154.0		
		161.7	+ 7.7
	154.0		
$1^h\ 31^m$	flame under copper tube		
	153.2		
		161.4	+ 8.3
	153.0		
		161.7	+ 8.7
	153.0		
		162.0	+ 9.2
	152.5		
		162.6	+ 9.8
	153.0	vapours appear	
		163.0	+ 10.0
	153.0		
		163.2	+ 10.2
	153.0	abundant vapours	
		163.5	+ 10.8
	152.7		
		163.7	+ 10.8
	153.0		
	flame removed		
	152.7		
		163.5	+ 10.8
	152.7		
	mercury at room temperature		
	154.0		
		162.1	+ 8.0
$1^h\ 41^m$	154.2		
$1^h\ 48^m$	155.2		
		162.8	+ 7.6
	155.2		

the deflections became less than without heating, showing the effect to be reversible.

In order to find out whether the deflection for unequal temperatures of the jets — maximum 3.2 mm. — could be ascribed to a chemical reaction between the mercury and the glass, we heated tube B for an hour with the pressure off, so as to give some of the mercury a much greater opportunity than in ordinary cases to form such a combination. Thus the mercury jet would have got different composition for the first minute of the experiment and a changed deflection would result. As we did not find any change in the deflection we cannot ascribe the observed effect to chemical contamination of the mercury.

Our effect may however be explained, as to magnitude and direction, by the thermo-electric force between mercury under pressure and mercury without pressure. This force was first observed by DES COUDRES [1]), and afterwards measured also by WAGNER and HÖRIG [2]). The mercury in our glass apparatus had the pressure of the compressed air, the mercury jets consisted of mercury at atmospheric pressure and their points of contact with the mercury at high pressure were at different temperatures.

We proved by a separate experiment that this explanation is the right one. We connected the tops of the tubes B by a short close-fitting glass knee, which was thus filled up by the mercury from the jets, a small aperture in the upper part serving as an overflow for the mercury. One of the tubes B now being heated, we obtained deflections of the same order as before, although there were no free mercury jets and therefore no sudden transition of temperature.

There is, however, one detail which remains unexplained in this way: we always found a greater effect for superficial contact of the jets than for a full contact. The difference increased with the difference in temperature and amounted to 15 mm. in maximo.

This phenomenon might be due to the increase of the temperature gradient at a superficial contact and then would prove the reality of BENEDICKS' so called fundamental effect. Of course one should not forget that this thermo-electric force amounts only to 3.5×10^{-8} Volt for the extremely steep fall of temperature of 300° over a distance less than 0.1 mm. Therefore this small force may be wholly neglected in all practical cases where it appears together with ordinary thermo-electric currents. We devised yet another experiment to demonstrate the minuteness — perhaps even the non-existence — of this effect of temperature fall, and to get rid of the disturbing pressure effect. A thin-walled glass tube was prepared, diameter outside 1.00 mm, inside 0.80 mm, and drawn down at the middle part to an outside diameter of 0.45 mm, inside diameter 0.30 mm. This tube was attached by short rubber tubes to the tubes B, from

1) DES COUDRES. Wied. Ann. **43**, p. 673, 1891.

2) E. WAGNER. Ann. d. Physik. **27**, p. 955, 1908.
H. HÖRIG, Ann. d. Physik **28**, p. 871 1909.

which the narrow tops had been cut off. A small difference of level on the two sides then sufficed to draw a slow current of mercury through the thin tube. Without this current we could not detect any deflection when the small tube was heated on either side of the constriction. Now the section of the mercury in the tube was 0.50 mm^2, of the glass walls 0 38 mm^2, and in the constriction 0.08 mm^2 and 0.10 mm^2 respectively. The thermal conductivity of mercury being ten times that of glass, the conduction through the latter could not be of any moment here, as it was in BENEDICKS' experiment. Besides we could greatly increase the sensitiveness of our test by having the mercury streaming against the flow of heat. Thus the cold mercury streamed through the constriction and was heated immediately afterwards by a Bunsen flame, which surrounded the bare glass tube. In this way the walls of the constriction were certainly kept cool by the flow of mercury, the velocity of which was six times that in the heated tube. A temperature difference of 250° over a distance of a few millimetres was thus obtained. The galvanometer did not show the slightest deflection while 0.1 mm could have been detected with certainty, the zero being extremely steady in this case. Therefore any effect caused by the temperature gradient mentioned should be less than 1.10^{-9} Volt.

The above mentioned difference of 1.5 mm for different kinds of contact of the jets may very well be explained without the assumption of a thermo-electric force depending on the temperature gradient. From the quantity of mercury delivered per minute and the diameter of the jet we found its velocity to be 5 metres per second. Therefore the time of contact of the jets was of the order of 10^{-5} sec., and a small part of the mercury is cooled in this short time from 300° to half this value. It may well be that in this mercury the internal equilibrium between the electrons and the metal is upset, which would cause it to behave thermo-electrically like a different substance. As this different substance would have unequal temperatures at the two ends, a thermo-electric current would be produced.

In our opinion this investigation therefore disproves the existence of an effect as described by BENEDICKS, and there is accordingly no ground for modifying the existing theory of thermo-electricity.

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