

COMMUNICATIONS
FROM THE
PHYSICAL LABORATORY

OF THE
UNIVERSITY OF LEIDEN

BY
H. KAMERLINGH ONNES,
Director of the Laboratory.

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**No. 120b.**  
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H. KAMERLINGH ONNES. "Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures."

(Translated from: *Verslagen van de Afdeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, 28 April 1911, p. 1479—1481).

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Probably the first report of superconductivity in mercury (at least in English). See "red box" in text, and note the acknowledgement to G. Holst who actually made the measurement, and, as I have been told, had the idea to purify Hg first by distillation.

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H. KAMERLINGH ONNES. "*Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures.*"

§ 1. *Introduction.* Since the appearance of the last Communication dealing with liquid helium temperatures (December 1910) liquid helium has been successfully transferred from the apparatus in which it was liquefied to another vessel connected with it in which the measuring apparatus for the experiments could be immersed — in fact, to a *helium cryostat*. The arrangements adopted for this purpose which have been found to be quite reliable will be described in full detail in a subsequent Communication. In the meantime there is every reason for the publication of a preliminary note dealing only with the results of the first measurements made with this apparatus, in which I have once more obtained invaluable assistance from Dr. DORSMAN and Mr. G. HOLST. These results confirm and extend the conclusions drawn from the previous experiments upon the change with temperature of the resistance of metals. Moreover, it was in the first place shown that liquid helium is an excellent insulator, a fact which has not hitherto been specifically established. This was of importance since the resistance measurements were made with naked wires, a method that is permissible only if the electrical conductivity of the liquid helium is inappreciable.

§ 2. *The resistance of gold at helium temperatures.* In the second place a link in the chain of reasoning which I adopted in § 3 of Communication N^o. 119 B to show that the resistance of pure gold is already inappreciable at the boiling point of liquid helium has been put to the test by determining the resistance in liquid helium of the gold wire Au_{III} which was then estimated by extrapolation on the analogy of the platinum measurements. Within the limits of experimental error which are indeed

greater for the present experiment than was the case for the others that value is now supported by direct measurement. The conclusion that the resistance of pure gold within the limits of accuracy experimentally obtainable vanishes at helium temperatures is hereby greatly strengthened.

§ 3. *The resistance of pure mercury.* The third most important determination was one of the resistance of mercury. In Communication No. 119 a formula was deduced for the resistance of solid mercury; this formula was based upon the idea of resistance vibrators, and a suitable frequency ν was ascribed to the vibrators which makes $\beta \nu = a = 30$ ($\beta = \text{PLANCK'S number } h/k = 4.864 \times 10^{-11}$). From this it was concluded:

1^o. That the resistance of pure mercury would be found to be much smaller at the boiling point of helium than at hydrogen temperatures, although its accurate quantitative determination would still be obtainable by experiment; 2^o. that the resistance at that stage would not yet be independent of the temperature, and 3^o. that at very low temperatures such as could be obtained by helium evaporating under reduced pressure the resistance would, within the limits of experimental accuracy, become zero.

Experiment has completely confirmed this forecast. While the resistance at 13.^o9 K is still 0.034 times the resistance of solid mercury extrapolated to 0^oC., at 4^o.3 K it is only 0.00225, while at 3^o K it falls to less than 0.0001.

The fact, experimentally established, that a pure metal can be brought to such a condition that its electrical resistance becomes zero, or at least differs inappreciably from that value, is certainly of itself of the highest importance. The confirmation of my forecast ¹⁾ of this behaviour affords strong support to the opinion to which I had been led that the resistance of pure metals (at least of platinum, gold, mercury and such like) is a function of the PLANCK vibrators in a state of radiation equilibrium. (Such vibrators were applied by EINSTEIN to the theory of the specific

¹⁾ In connection with its deduction it is to be noted that the gold-silver thermo-element behaved in liquid helium quite so as the experiments in liquid hydrogen (KAMERLINGH ONNES and CLAY, Comm. No. 107b) made expect.

heats of solid substances, and by NERNST to the specific heats of gases).

With regard to the value of the frequency of the resistance vibrators assumed before (one could try to obtain frequencies from resistances) it is certainly worth noting that the wave-length in vacuo which corresponds with the period of the mercury resistance vibrators is about 0.5 m.m. while RUBENS has just found that a mercury lamp emits vibrations of very long wave-length of about 0.3 m.m. In this way a connection is unexpectedly revealed between the change with temperature of the electrical resistance of metals and their long wave emission.

The results just given for the resistance of mercury are, since they are founded upon a single experiment, communicated with all reserve. While I hope to publish a more detailed description of the investigation which has led to these results in the near future, and while new experiments are being prepared, which will enable me to attain a greater degree of accuracy, it seemed to me desirable to indicate briefly the present position of the problem ¹).

¹) That this is justified is apparent from important papers which I have just received as this goes to press; in one NERNST extends the investigation referred to in Comm. No. 119 of the specific heats and is also independently led to assure a connection between the energy of vibrators and electrical resistance, and in the other this hypothesis is further developed by LINDEMANN.

of deductions regarding relative values. With $\alpha = 0.00105$, the mean of the values obtained by CURIE with samples which were not perfectly pure, extrapolating to $20^{\circ}.3$ K. we should obtain $\chi_{20.3} = -1.64 \times 10^{-6}$ which is a value rather greater than that given by experiment. It would therefore appear that the linear change of the magnetisation of bismuth does not go on as the temperature falls, and this result is also in agreement with the experiments of FLEMING and DEWAR, who only went as far as liquid air. The two values which we obtained in hydrogen boiling under reduced pressure seem to indicate that when the temperature sinks as low as this, the susceptibility becomes pretty well *independent* of the temperature; if the law of change were still linear at these temperatures then between $20^{\circ}.3$ K. and $13^{\circ}.9$ K. one should have to observe an increase of 0.7% , while what was actually observed was rather a decrease.

Hydrogen. With a view to the determination of the corrections to be applied we made a measurement of the susceptibility of liquid hydrogen, the result of which probably deviates less than 10% from the true value. This determination is rendered extremely difficult by the smallness of the density and of the volume-susceptibility of the hydrogen. We found for the volume-susceptibility $K = -0.186 \times 10^{-6}$ and, taking DEWAR's value for the density of liquid hydrogen 0.07 we find $\chi = -2.7 \cdot 10^{-6}$. Within the limits of experimental error this value agrees with that calculated by PASCAL ¹⁾ $\chi = -3.0 \times 10^{-6}$ from the organic compounds. As we do not in the meantime propose to repeat this determination we feel that there is sufficient reason for us to communicate the result here.

¹⁾ P. PASCAL. Ann. chim. phys. (8) 19 (1910) p. 5.

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**No. 122b.**

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H. KAMERLINGH ONNES "Further Experiments with Liquid Helium. D. On the Change of the Electrical Resistance of Pure Metals at very low Temperatures, etc. V. The Disappearance of the resistance of mercury".

(Translated from: *Verslagen van de Afdeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, 27 Mei 1911. p. 81-83).

H. KAMERLINGH ONNES. *"Further Experiments with Liquid Helium. D. On the Change of the Electrical Resistance of Pure Metals at very low Temperatures, etc. V. The Disappearance of the resistance of mercury."*

As mentioned in a former Communication (April 1911) I have made a more accurate examination of the resistance of pure mercury at helium temperatures, in which I have once more had the assistance of Messrs. DORSMAN and HOLST. The resistance was now measured with the differential galvanometer by the method of overlapping shunts (KOHLRAUSCH) and also by the method of the measurement of current strength and of potential difference. By this it was confirmed that at 3° K. the value of the resistance sinks to below 0.0001 times the value of the resistance of solid mercury at 0° C. extrapolated from the melting point. But from the present measurements it has also been ascertained that the actual value of the resistance is very much smaller than this upper limit which I was able to ascribe to it from my former measurements.

The value of the mercury resistance used was 172.7 Ω in the liquid condition at 0° C.; extrapolation from the melting point to 0° C. by means of the temperature coefficient of solid mercury gives a resistance corresponding to this of 39.7 Ω in the solid state. At 4° 3 K. this had sunk to 0.084 Ω , that is, to 0.0021 times the resistance which the solid mercury would have at 0° C. At 3° K. the resistance was found to have fallen below 3×10^{-6} Ω , that is, to one ten-millionth of the value which it would have at 0° C. As the temperature sank further to 1° 5 K. this value remained the upper limit of the resistance.

The next step was obviously to look for the point at which the resistance first becomes measurable as the temperature is raised. The temperature of this point was found to be slightly more than 4° 2 K. at which the resistance was found to be 230

micro-ohms or one hundred thousandth of the resistance (solid) at 0° C. As the temperature was raised to that of the boiling point (4° 3 K.) the resistance rose once more to 0.084 Ω . This change took place more quickly than the rate of change to which the formula given in the December (February) Communication leads—exactly how much more quickly is not yet known but it certainly seems to increase very much more rapidly. A point of inflection which does not appear in the formula given—a formula which I regarded as incomplete also on account of the method by which it was deduced—seems to occur between the melting point of hydrogen and the boiling point of helium in the curve which represents the resistance as a function of T .

The more the upper limit which can be ascribed to the resistance remaining at helium temperatures decreases, the more important becomes the observed phenomenon that the resistance becomes practically zero. When the specific resistance of a circuit becomes a million times smaller than that of the best conductors at ordinary temperatures it will, in the majority of cases, be just as if electrical resistance no longer existed under those conditions. If conductors could be obtained which could be regarded as being devoid of resistance as long as their cross section was not excessively small, or conductors of the smallest possible sections, either cylindrical with diameters of the order of the wave length of light, or films of molecular thickness, whose resistance would be but small, if there had no more to be reckoned with the JOULE development of heat in increasing the current in a bobbin to exceedingly high values because the development of heat in a circuit of constant current strength could be made extremely small compared with the latent heat of vaporization of the liquid which can be used for cooling, — then further experiments in all possible directions would give the fullest promise, notwithstanding the great difficulties which are encountered when working with liquid helium. It is therefore all the more necessary to establish beyond all possibility of doubt the property of which advantage would be taken in such experiments. With this end in view modified measurements are now being made.

It is further worth noting that just as the resistance of constantin changed but little when the temperature fell from ordinary

to liquid hydrogen temperatures so too the change is slight as the temperature sinks further to those of liquid helium. This property was utilised to obtain rough confirmation of the value of the latent heat of vaporization of helium which can be calculated from CLAPEYRON'S formula using the data already published concerning its vapour pressure and vapour density. (Compare the above remarks as to the ratio between the JOULE heat development to the latent heat of the liquid which is used for cooling).

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**N<sup>o</sup>. 124c.**



**H. KAMERLINGH ONNES.** — "Further Experiments with Liquid Helium. G. On the Electrical Resistance of Pure Metals, etc. VI On the Sudden Change in the Rate at which the Resistance of Mercury Disappears." (*With a plate.*)

(*Translated from: Verslagen van de Afdeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam, 30 December 1911, p. 799—802.*)



H. KAMERLINGH ONNES. — *Further Experiments with Liquid Helium. G. On the Electrical Resistance of Pure Metals, etc. VI. On the Sudden Change in the Rate at which the Resistance of Mercury Disappears.*"

(Communicated in the meeting of November 25, 1911).

§ 1. *Introduction.* In Comm. N<sup>o</sup>. 122*b* (May 1911) I mentioned that just before this resistance disappeared practically altogether, its rate of diminution with falling temperature became much greater than that given by the formula of Comm. N<sup>o</sup>. 119. In the present paper a closer investigation is made of this phenomenon.

§ 2. *Arrangement of the resistance.* A description was given in Comm. N<sup>o</sup>. 123 (June 1911) of the cryostat which, by allowing the contained liquid to be stirred, enabled me to keep resistances at uniform well-defined temperatures; and in that paper I also mentioned that measurements of the resistance of mercury at the lowest possible temperatures had been repeated using a mercury resistance with mercury leads. The immersion of a resistance with such leads in a bath of liquid helium was rendered possible only by the successful construction of that cryostat.

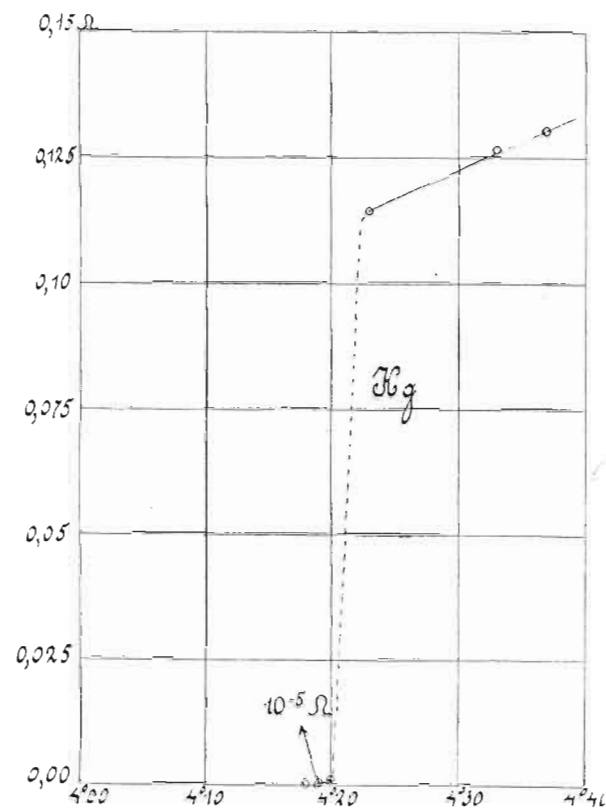
The accompanying Plate, which should be compared with the Plate of Comm. N<sup>o</sup>. 123, shows the mercury resistance with a portion of the leads; it is represented diagrammatically in fig. 1. Seven glass *U*-tubes of about 0.005 sq. mm. cross section are joined together at their upper ends by inverted *Y*-pieces which are sealed off above, and are not quite filled with mercury; this gives the mercury an opportunity to contract or expand on freezing or liquefying without breaking the glass and without breaking the continuity of the mercury thread formed in the seven *U*-tubes. To the *Y*-pieces  $b_0$  and  $b_8$  are attached two leading tubes  $Hg_1$ ,  $Hg_2$  and  $Hg_3$ ,  $Hg_4$  (whose lower portions are shown at  $Hg_{10}$ ,

$Hg_{20}$ ,  $Hg_{30}$ ,  $Hg_{40}$ ) filled with mercury which, on solidification, forms four leads of solid mercury. To the connector  $b_4$  is attached a single tube  $Hg_5$ , whose lower part is shown at  $Hg_{50}$ . At  $b_0$  and  $b_8$  current enters and leaves through the tubes  $Hg_1$  and  $Hg_4$ ; the tubes  $Hg_2$  and  $Hg_3$  can be used for the same purpose or also for determining the potential difference between the ends of the mercury thread. The mercury filled tube  $Hg_3$  can be used for measuring the potential at the point  $b_4$ . To take up less space in the cryostat and to find room alongside the stirring pump  $Sb$ , the tubes which are shown in one plane in fig. 1 were closed together in the manner shown in fig. 2. The position in the cryostat is to be seen from fig. 4 where the other parts are indicated by the same letters as were used in the Plate of Comm. N<sup>o</sup>. 123. The leads project above the cover  $Sb_1$  in a manner shown in perspective in fig. 3. They too are provided with expansion spaces, while in the bent side pieces are fused platinum wires  $Hg_1'$ ,  $Hg_2'$ ,  $Hg_3'$ ,  $Hg_4'$ ,  $Hg_5'$  which are connected to the measuring apparatus. The apparatus was filled with mercury distilled over in vacuo at a temperature of 60° to 70° C. while the cold portion of the distilling apparatus was immersed in liquid air.

§ 3. *Results of the Measurements.* The junctions of the platinum wires with the copper leads of the measuring apparatus were protected as effectively as possible from temperature variation. The mercury resistance itself with the mercury leads which served for the measurement of the fall of potential seemed, however, on immersion in liquid helium to be the seat of a considerable thermo-electric force in spite of the care taken to fill it with perfectly pure mercury. The magnitude of this thermo-electric effect did not change much when the resistance was immersed in liquid hydrogen or in liquid air instead of in liquid helium, and we may therefore conclude that it is intimately connected with phenomena which occur in the neighbourhood of the transition of solid to liquid mercury. A closer investigation of the true state of affairs was postponed for the meantime, and the thermoelectric force was directly annulled during the measurements by an opposed electromotive force taken from an auxiliary circuit. The magnitude of this thermoelectric force, which for one pair of the leads came to

about half a millivolt, made it impracticable to reverse the auxiliary current as is usually done in the compensation method. The resistance of the mercury thread was then obtained from the differences between the deflections of the galvanometer placed in circuit with  $Hg_2$  and  $Hg_3$  and the compensating electromotive force, when the main current passing through the resistance was reversed. The galvanometer was calibrated for this purpose.

In the accompanying figure is given a graphical representation of the resistances observed <sup>1)</sup>.



<sup>1)</sup> For the resistance of the solid mercury at 0° C. extrapolated from the melting point nearly 60 Ohm can be accepted. In the solidifying process differences occur which make necessary special measurements to be able to give the exact proportion of the resistance of the wire at

As a former experiment showed that there was a pretty rapid diminution of the resistance just below the boiling point of helium, there arose in the first place a question as to whether there exists between the melting point of hydrogen and the boiling point of helium a point of inflection in the curve which represents the resistance as a function of the temperature. The temperature of the bath was therefore raised above the boiling point by allowing the pressure under which the liquid evaporated to increase, an operation possible with this cryostat by closing the tap  $Lak_2$ , leading to the liquefier. The excess pressure was read on an oil manometer connected to  $S_3$ . These measurements showed that from the melting point of hydrogen to the neighbourhood of the boiling point of helium the curve exhibited the ordinary gradual lessening of the rate of diminution of resistance, practically the same as given by the formula of Comm. N<sup>o</sup>. 119. A little above and a little below the boiling point, from  $4^{\circ}.29$  K. to  $4^{\circ}.21$  K. the same gradual change was clearly evident (cf. the fig.), but between  $4^{\circ}.21$  K. and  $4^{\circ}.19$  K. the resistance diminished very rapidly and disappeared at  $4^{\circ}.19$  K. (Temperature measurements are here given with  $4^{\circ}.25$  K. as the boiling point of helium).

During the discussion initiated by the communication of these results to the Brussels "Conseil SOLVAY" (2 Nov. 1911) M. LANGEVIN asked if other properties of the substance displayed similar sudden changes, as would be the case if mercury underwent a structural modification at  $4^{\circ}.20$  K. Experiments with the object of settling this point were, of course, immediately planned when this phenomenon was observed, but they have not yet been concluded. It can well be, however, that, should there exist such a new modification, it would differ from ordinary mercury at higher temperatures chiefly by the property that the frequency of the vibrators in the new state has become greater, and therefore the conductivity rises to the extremely large value exhibited below  $4^{\circ}.19$  K.

§ 4. *The motion of electricity through mercury at temperatures*

helium temperatures to that at  $0^{\circ}$  C. (solid extrapolated from the melting point). Therefore here are given the resistances themselves. [Note added in the translation.]

*below*  $4^{\circ}.19$  K. The next step was as in the earlier experiments to try by sending a comparatively strong current through the resistance, to obtain an upper limit to the value which must be ascribed to the resistance when this has practically vanished as is the case at  $3^{\circ}.5$  K. The peculiarities of the phenomena which then occur make it desirable to experiment first with a modified apparatus before proceeding further.

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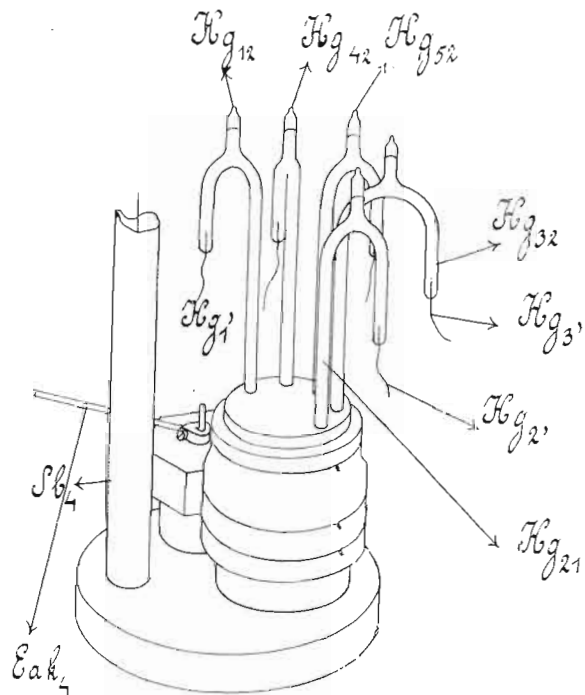


Fig. 3.

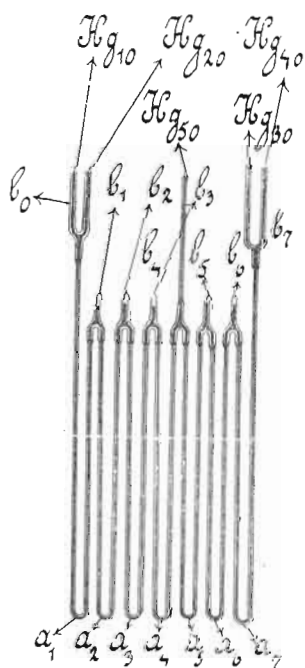


Fig. 1.



Fig. 2.

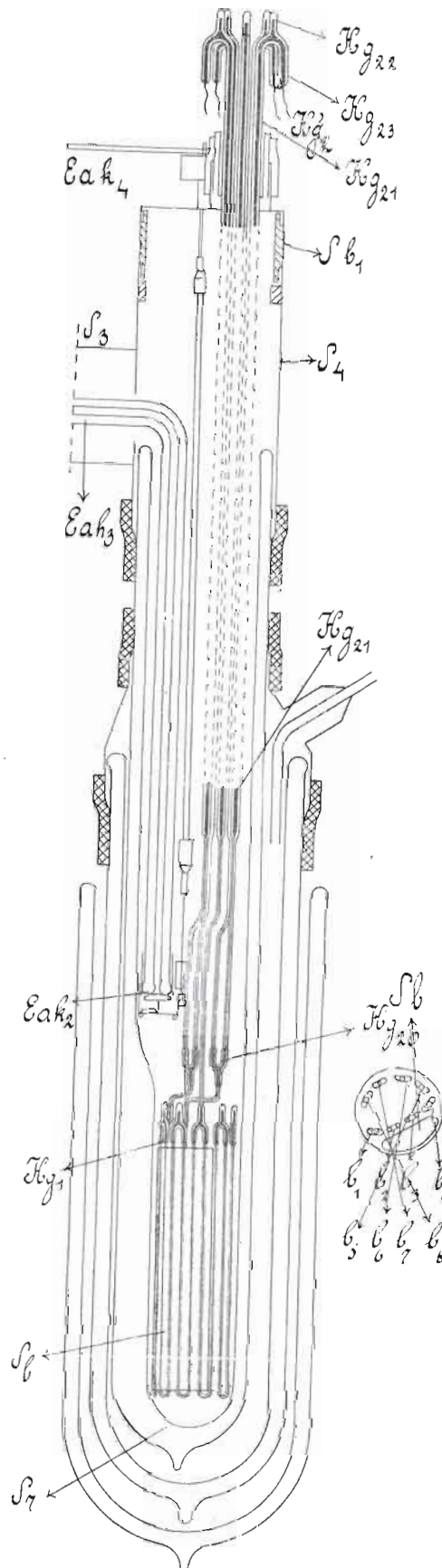


Fig. 4.