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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, in: KNAW, Proceedings, 14 II, 1911-1912, Amsterdam, 1912, pp. 818-821
decide, a theory of course which first of all takes account of the fundamental chemical facts which we mentioned above, but which further succeeds in avoiding the drawbacks — particularly with respect to the specific heats — which adhere to the hypothesis on the chemical forces sketched more at length in our previous paper. And then it cannot be doubtful, in our opinion, by what way we shall have to try to find such a theory. We shall have to extend the theory of indivisible units of energy, which has led to such remarkable results, to the chemical phenomena; it will be necessary to investigate in what way the properties of the reversible chemical reactions are connected with the phenomena of radiation. When this connection has been found, the course is indicated to calculate the difference of entropy of a chemical reaction by the aid of the statistical theory of entropy at temperatures at which this reaction can actually take place, and then it will be very simple to calculate by the aid of the acquired knowledge of the specific heats the difference of entropy also for temperatures, at which there can no longer be question of chemical reactions.

One of us has been occupied with this question, and hopes to be able before very long to publish further communications on this subject.


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

§ 1. Introduction. In Comm. N°. 122b (Proc. 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°. 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°. 123 (Proc. 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°. 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 $b,$ and $b_{s}$ are attached two leading tubes $Hg_{1},$ $Hg_{2},$ and $Hg_{3},$ $Hg_{4},$ (whose lower portions are shown at $Hg_{10},$ $Hg_{10},$ $Hg_{10},$ $Hg_{10}$) filled with mercury which, on solidification, forms four leads of solid mercury. To the connector $b_{2}$ is attached a single tube $Hg_{3},$ whose lower part is shown at $Hg_{30}.$ At $b_{6}$ and $b_{s}$ current enters and leaves through the tubes $Hg_{1}$ and $Hg_{4};$ the tubes $Hg_{1}$ and $Hg_{4}$ 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 $Hg_{1}$ 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 $Sb_{1},$ 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°. 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 $Hg'_{1},$ $Hg'_{2},$ $Hg'_{3},$ $Hg'_{4},$ 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 neigh-
bourhood 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 $H_g$, and $H_g$, 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 ¹).

¹) For the resistance of the solid mercury at $0^\circ$ 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 helium temperatures to that at $0^\circ$ C. (solid extrapolated from the melting point). Therefore the resistances themselves are given here. [Note added in the translation].
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 $Eak_2$, leading to the liquefier. The excess pressure was read on an oil manometer connected to $S_2$. 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°. 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 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 $3,25$ K. The peculiarities of the phenomena which then occur make it desirable to experiment first with a modified apparatus before proceeding further.