simples comme ceux de M. NERNST et de M. HENNING, en se bornant chaque fois à des cas spéciaux et des domaines restreints. Les thermomètres auxiliaires prendront d'autant plus d'importance que l'échelle des ... ore de p... on. Obt...

Il ... m- pris... elle des ... na- tiqu... urs auss... les bass... nts de ... era l'out... urs des ... le dom... an- donner le domaine supérieur, il pourra continuer de son côté à concentrer surtout ses forces sur le domaine des températures plus difficilement accessibles que celles dont on dispose déjà régulièrement ailleurs. Nous avons donc le droit d'espérer que, par une division de travail et par une coopération heureuses, notre commission contribuera à donner une base solide à la thermométrie des basses températures.

A summary of Leiden Communications 133-144 presented at the 3rd International Conference on Refrigeration, Washington-Chicago, September-October 1918 (how did the participants travel during WWI?). It represents a fascinating and eloquent personal narrative of the activities at Leiden from 1911 to 1918. For example, Onnes acknowledges on p. 50, footnote 1), the financial contributions of an American utility company to the work at Leiden. And go to page 60 and read Onnes' "ectasy" regarding the initial measurements on Hg in 1911.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

SUPPLEMENT N°. 34*b*

to N°. 133—144.

H. KAMERLINGH ONNES. Report on researches made in the Leiden cryogenic laboratory between the Second and Third International Congress of Refrigeration.

(*Reprinted from: Notes on the Work of the Section for physics, chemistry and thermometry of the first international commission of the Association Internationale du Froid, presented at Third International Congress of Refrigeration, Washington-Chicago*, Sept. 15 to Oct. 1, 1913.)

EDUARD IJDO - PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Report on researches made in the Leiden cryogenic laboratory between the Second and Third International Congress of Refrigeration.*

NOTES ON THE WORK OF THE SECTION FOR PHYSICS, CHEMISTRY AND THERMOMETRY OF THE FIRST INTERNATIONAL COMMISSION OF THE ASSOCIATION INTERNATIONALE DU FROID.

VI.

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§ 1. **Introduction.** For my Report on work done in the Leiden laboratory since the last congress, I shall select, just as I did at Vienna, some subjects, that give an idea of the principal problems with which we are occupied and of the methods applied to their solution. I may go somewhat further now in the limitation of my choice because in the Report given to the Comité de Patronage and in the preceding "Notes on the Work of the Section of Physics, etc." part of the work regarding the thermometry of low temperatures and the equation of state has been already dealt with. This limitation agrees well with my wish to bring before you some experimental results, at which we have arrived and which seem of importance for our insight in the fundamental properties of matter. Among these there are some which have raised new problems, problems for the solution of which experimental work at low temperatures, in particular also at the lowest temperatures, seems to be required in the first place.

I shall dwell especially at some length on the new field of research that is opened by the discovery of the superconductive state of metals.

§ 2. **Radioactivity remains the same at the lowest temperatures.** Work at hydrogen temperatures continues to take a prominent place in the laboratory. An improvement of the hydrogen-liquefier realising a better regeneration of cold by the introduction of an auxiliary regenerator according to the plan developed in 1906 [1]), has much contributed to the possibility of maintaining with certainty constant hydrogen-temperatures for weeks. Under these circumstances all kinds of radio-active phenomena can be investigated at these low temperatures. Madame CURIE did me the honour to accept my collaboration for this purpose. A first research, which did not yet require the extensive means referred to, has been completed [2]).

It had in view one of the most remarkable peculiarities of radio-active substances viz. that the radiation is independent of the temperature. This fact is related to the fact that the radio-active constants do not change with temperature, as according to the theory of radio-active transformation the intensity of radiation of a simple substance is proportional to the rapidity of the transformation. The fact is of the highest importance, so that it was desirable to enlarge the results already obtained by extending the experiments to a wider range of temperature and by increasing the accuracy of the measurements, which in the existing investigations could not have been greater than 1 °/₀ at most. We have succeeded in descending to the temperature of liquid hydrogen and the accuracy of the results obtained may be placed at 0.1 °/₀.

The preparatory experiments were partly made in Paris and partly in Leiden, while the final experiments were made by Madame CURIE and me in Leiden.

The measurements were concerned with the penetrating radiation of radium. By using a compensation method it was possible to determine very slight changes in the radio-active intensity. The results within the limits of accuracy do not confirm the existence of a quickly acting influence upon the radiation. Cooling radium down to the temperature of liquid hydrogen during a period of not more than

[1]) The general idea of this regenerator was given in the paper containing the description of the Leiden cycle for continuous work with liquid hydrogen. A full description of the apparatus in working order will be given before long.

[2]) Madame P. CURIE and H. KAMERLINGH ONNES, The radiation of radium at the temperature of liquid hydrogen. Leiden Comm. No. 135.

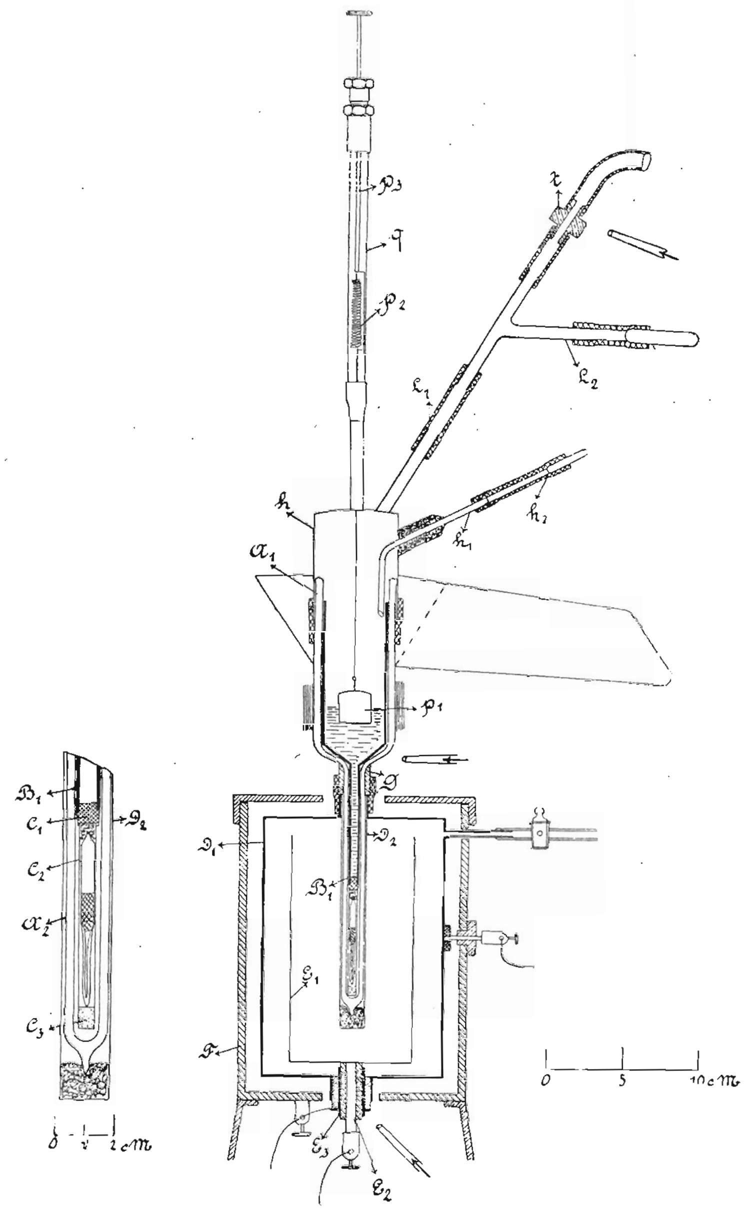


Fig. 1.

$1\,^1/_2$ hours does not cause a change in the gamma-radiation of 1 in 1000. In one experiment that was particularly successful, the change was even less than 1 in 5000. It is thus probable, paying due regard to the degree of accuracy attained, that this decrease of temperature has *no immediate* or *quickly decernable* influence upon the emanation or the active deposits of short period (radium *A*, *B* and *C*).

The apparatus which was used is given in fig. 1. It consists of a vacuum-glass *A* in which a copper vessel *B* is placed, which contains the low temperature bath.

The vacuum glass consists underneath of a tube-shaped portion. The copper vessel which fits into the vacuum glass, is also provided with a tube-shaped portion, which is closed underneath, at B_1, by a metal stopper to which a tube of thin aluminium is attached; this tube contains a sealed glass tube with radium, which is cooled in this manner to the temperature of the bath without being in contact with the liquid. The penetrating rays that the radium in the tube sends out penetrate through a metal wall into the ionisation chamber.

This consists of a cylindrical box D_1 which is connected to a battery; in the middle of the lid of this space a tube D_2 is soldered which is closed at the lower end. The tube D_2 has thick walls to make sure that only the most penetrating rays were used.

The insulated electrode E_1 which is a hollow cylinder is connected with the electrometer. When the apparatus is mounted the tube-shaped portion of the vacuum-glass is inside the tube D_2, on which it is fitted by a piece of amber sealed to the vacuum-glass and a thick piece of india-rubber. When the tube containing the radium is in its place, ions are formed on both sides of the electrode E_1 in the air that fills the box D_1. The current that is taken up by this electrode is measured by an electrometer and a plate of piezo-quartz.

The experiment consists in measuring the ionisation current generated by the rays of the radium: 1⁰. when the radium is at the temperature of the room, and 2⁰. when the radium is cooled to the temperature of liquid hydrogen. The ionisation chamber which is outside the vacuum-glass remains at about the temperature of the

room. The chamber is air-tight, and the quantity of gas that it contains does not alter during the experiments. The accuracy of

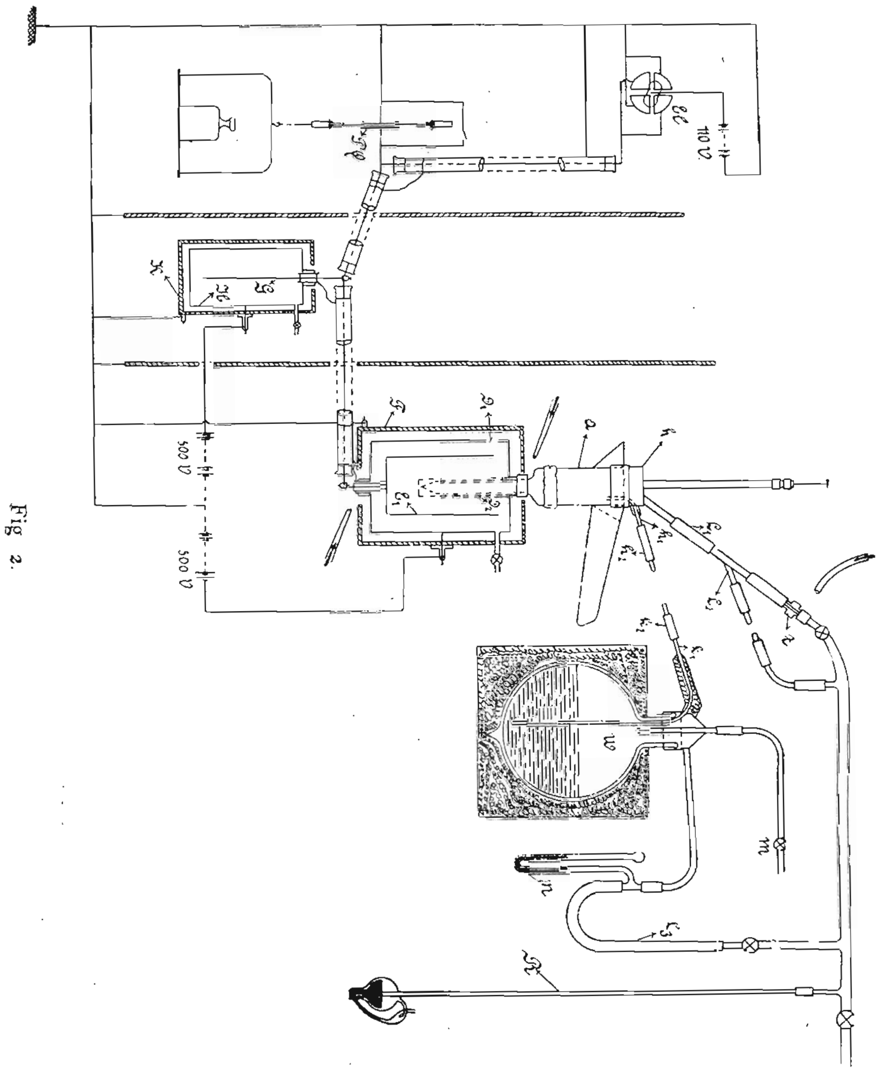


Fig. 2.

the measurements is, as was said before, greatly increased by using a compensation method. This consists in compensating the current to be measured by a current in the opposite direction which is generated in a second ionisation chamber by a tube containing radium, which is kept at constant temperature during the experiments. When working with penetrating rays the current is approximately proportional to the amount of ionised air. The ionisation chamber like the principal one is therefore hermetically closed

We had to take very great precautions to prevent the cryogenic operations from causing insulation errors in consequence of the precipitation of moisture from the surrounding air. The arrangement of the apparatus, with the cryostat completely closed, allowed this and ensured moreover, that the radium tube could only come in contact with the gaseous phase of the liquefied gas and that when this was hydrogen no solid air could be deposited on the tube. The research exemplified once more the advantage of the method of working with liquid hydrogen adopted at Leiden, i. e. working with closed apparatus, which can be evacuated, and syphoning the liquid hydrogen from a reserve globe into the cryostat by means of a temporary connection made by a small tube of india-rubber, reserve globe and cryostat being connected to a gasometer with pure hydrogen To prevent the influence of vibrations on the arrangement of the finely granular salt in the not quite filled tube, the india-rubber connecting tube was this time taken extra long.

Besides the amber piece g, of which I have spoken. there is an amber piece in the exhaust (comp. fig. 2); to prevent this piece of amber being cooled too much in the filling. the cold vapours are carried off by a supplementary tube L_2, which is coupled off as soon as the filling is completed. When the evaporation of the bath has become stationary, a current of air a little warmer than that of the room directed upon the amber is sufficient to maintain insulation. A float suspended to a weak spring p_2 that can be moved up and down ensures, that in filling the copper vessel B the liquid gas does not overflow, as it might penetrate into the cooling chamber, which would give rise to irregularities and might injure the radium tube. It serves also to read at any moment by the shortening or elongation of the spring the height of the level of the liquid.

I hope the details. which I have given, suffice to give an idea of

the experiments which led to the interesting result, formulated in the beginning of this section.

§ 3. **Deviations from Curie's law becoming sensible at low temperatures. Negative molecular field and number of magnetons for deviating paramagnetic substances.** The importance of low temperature research for the study of paramagnetism, which I pointed out at the Vienna congress, has been much emphasized by the discovery of the magneton by Weiss. This discovery has given a great interest to the study of the deviations from Curie's law. According to the theory of Langevin the molecules of paramagnetic substances contain elementary magnets of constant moment. Heat agitation of rotatory motion by turning the molecules opposes the orientation of these magnets in the direction of the impressed field and will bring about, that in a gas or diluted solution the susceptibility in relatively weak fields is inversely as the kinetic energy of the rotation of the molecules. This kinetic energy is put proportional to the absolute temperature. We shall have to return to this assumption. If it is accepted, the reciprocal susceptibility of a gas or diluted solution will be proportional to the absolute temperature. The theory may be extended to liquid and solid substances, if the molecules have no rotational potential energy. Ferromagnetism according to Weiss is produced by a molecular field that depends on certain unknown mutual actions of the magnetic molecules. It is proportional to, but enormously greater than the impressed field under the action of which it comes into existence. At liquid hydrogen temperatures the effect of the heat agitation is insensibly small in comparison with that of the enormous molecular field that accompanies saturation of ferromagnetic substances. All elementary magnets under these circumstances are directed parallel to the field. If we then divide the magnetization at saturation by the number of molecules per unit of volume, we get the value of the moment of each elementary magnet. As reported at the Vienna congress, Weiss and I have obtained the data to calculate in this way the moments of the elementary magnets of some ferromagnetic substances. Weiss's discovery showed, that all elementary magnets are multiples of the magneton; the elementary iron magnet according to the above mentioned measurements, from which the value of the magneton can be very accurately determined, contains 11 and that of nickel 3 magnetons, the magneton-gramme having a magnetic moment of 1123.5.

The number of magnetons for each substance can be calculated from one determination of the susceptibility and the susceptibility at any temperature would be completely determined by this number, if the substance obeys the law of CURIE. Now this is in general not the case. In a research of PERRIER and me, on which I reported at the Vienna congress, it was shown that oxygen, which at higher temperatures in the gaseous state follows the law of CURIE, deviates from this law when at low temperatures it has passed into the liquid or the solid state.

Our research was extended afterwards [1]) to paramagnetic salts with a view to discovering a general law for the deviations from the law of CURIE, which present themselves at low temperatures: in the mean time came WEISS's discovery of the magneton, which required also the knowledge of the law we were seeking. Experience brought us to the conception, that in paramagnetism there exist corresponding states analogous to those found by WEISS for ferromagnetic substances and that this general law could be obtained by combining our experiments on different substances. The susceptibility of substances, which obey CURIE's law at ordinary temperatures, we concluded in this way, will in general, if the temperature is sufficiently lowered, begin to increase less rapidly than they should in accordance with the CURIE law, and continue to do so, until a maximum of susceptibility is reached after which a decrease sets in. The individual temperatures at which the deviations become appreciable and reach the same procentual value, differ considerably for the different substances, and were put proportional to the temperature of the maximum of susceptibility, which in consequence differs also considerably. We succeeded in finding, in crystallized gadolinium sulphate, a substance which follows the law of CURIE down to the freezing point of hydrogen. Apparatus is now nearly ready with which I hope to try, if this substance can be cooled to

[1]) KAMERLINGH ONNES and PERRIER. Leiden Commun. n⁰. 122*a*, 124*a*.

helium temperatures before a maximum of susceptibility is reached [1]).

The research was continued at hydrogen temperatures by Dr. OOSTERHUIS and me [2]). We discovered saturation phenomena in ferric sulphate very interesting in themselves, but on which I will not dwell here. By seeking for a CURIE point, using the reciprocal susceptibility, we found that the deviations from the law of CURIE for different salts and even for liquid oxygen could within the limits of accuracy be attributed to a negative or diamagnetic molecular field, i. e. the reciprocal susceptibility is proportional to the absolute temperature augmented by a certain constant quantity. WEISS and FOËX had arrived at a negative molecular field also in the case of γ iron and nickel alloys. The negative field, therefore, constitutes a new link between paramagnetic and ferromagnetic substances. The intensity of this negative molecular field proved to be much greater in the same salt, if it was taken anhydrous then when it was crystallized with a certain number of molecules of water. This was ascribed to the influence of the distance of the paramagnetic atoms on the value of the negative molecular field. The question of the negative molecular field seems to have been much advanced from the experimental side by a recent not yet published investigation by prof. PERRIER and me, that we planned long ago with a view to testing, whether the deviation of the susceptibility of liquid oxygen could be explained by the association of the ordinary oxygen molecules to less susceptible double molecules. We hoped to get information on this point by measuring the susceptibility of oxygen diluted with nitrogen. We have now reached a very interesting result. The deviation does not depend on temperature alone but also on density [3]). Strongly diluted oxygen, when compared at the same effective density i. e. with the same number of molecules in the same volume, followed the law of CURIE [4]) and diluted oxygen with greater effective density follows the

[1]) Saturation phenomena that are obtained by simple orientation of the elementary magnets without the molecular field coming into play, to which I alluded at the Vienna congress, may then be found perhaps in intense fields.

[2]) H. KAMERLINGH ONNES and E. OOSTERHUIS. Leiden Commun. n⁰. 129*b*.

[3]) If the deviation had been found independent of density this would have shown that it depends on the properties of the molecule of oxygen itself.

[4]) This result is obtained by extrapolation. There remains a small difference on which I will not dwell.

generalized law containing the constant of the negative field, when the molecular field peculiar to each effective density is taken into account The number of magnetons, when the correction for the molecular field is applied, is found the same as that determined by WEISS and PICARD at ordinary temperatures starting from the fact that for temperatures above 0° C. oxygen follows the law of CURIE according to CURIE's measurements. OOSTERHUIS and I had arrived at the result that gaseous oxygen continues to do so down to temperatures as low as — 120° C. [1]) The fact that the simple assumption of the negative molecular field leads in all these cases to the same number of magnetons seems a strong argument in favour of the magneton as well as for the conception of the negative molecular field depending on density.

I will not dwell here on the more complicated case of liquid oxygen itself and on the law of the dependency of the molecular field upon the density. I wished to draw attention to the interest that the study of oxygen, an element that can be investigated in the gaseous and the liquid and the solid state and that as liquid at low temperatures can be diluted with the diamagnetic liquid nitrogen in all proportions, has for the study of paramagnetism. It seems that it will be possible to find out by direct determinations the influence of the density or what comes to the same the influence of the distance of the molecules on the value of the negative molecular field with and without the interposition of another medium. One of the first things to do is therefore to determine the susceptibility of gaseous and liquid oxygen at and near the critical density.

We have till now followed the experimental line and left aside the explanation of the molecular field, accepting it (within the limits of the experiments and of their precision,) just as we accept the magneton, as an expression of well established experimental facts. But the name of molecular field itself conveys the idea that it is ascribed to forces exerted by the molecules.

It is interesting that it seems possible to explain the deviations of the law of CURIE which we represented by the negative molecular

[1]) H. KAMERLINGH ONNES and E. OOSTERHUIS. Leiden Comm. n°. 134*d*.

field without introducing any forces. This is done by OOSTERHUIS [1]). He takes in LANGEVIN's theory the kinetic energy of the rotatory energy of the molecules not proportional to the absolute temperature, but to the mean energy of rotation accepted by EINSTEIN and STERN [2]) for the explanation of the change of specific heat of gaseous hydrogen with temperature. [3])

As according to these physicists the energy of rotation tends to a constant value at decreasing temperatures, the reciprocal susceptibility, which according to LANGEVIN's theory is proportional to it, does the same. So OOSTERHUIS finds that the scheme of corresponding states of paramagnetism, of which I have spoken before, can be explained (leaving out of account susceptibility and the deviation from the law of CURIE increasing with temperature) and that even the behaviour of different elements as found by DU BOIS, HONDA and OWEN at higher temperatures can be made to fit in [4]).

[1]) E. OOSTERHUIS, Leiden Comm. Suppl n°. 31.

[2]) In order to get a fairly good agreement with the experimental results these physicists were led to the supposition, that at the absolute zero of temperature the rotations of the molecules have not come to rest, but that there the molecules still have in the mean a quite definite quantity of rotatory energy, dependent upon the moment of inertia which comes into play. In this way PLANCK's theory of radiation in the form in which the author has given it recently *viz.* continuous absorption and discontinuous emission, in which the vibrators have a zero-point energy, received firm support from an unexpected side. We will meet this zero energy again in the theories connected with the following subjects which I have to discuss.

[3]) The research of magnetism is — since WEISS — very closely connected with that of specific heat. I will remark therefore here that work on specific heat at the lowest temperatures is progressing at Leiden and that the specific heat of paramagnetic substances will be determined.

At the conseil-SOLVAY mention was made of the endeavours of Dr. KEESOM and me to overcome the difficulties of determining the ratio of the specific heats of gaseous hydrogen of small density at hydrogen temperatures.

In the mean time EUCKEN, working with compressed hydrogen, has obtained the highly important result we sought for. The completing of our research, which remains of interest, was retarded, but we hope to give it before long. A paper on the specific heat of lead at hydrogen temperatures by KAMERLINGH ONNES and KEESOM and another on the specific heat of mercury at helium temperatures by KAMERLINGH ONNES and HOLST will soon be published

[4]) I will add the remark, that EINSTEIN and STERN for simplicity's sake assume,

If this explanation should be further confirmed, the character of the negative molecular field is totally different from that of the positive molecular field, with which it is otherwise quite analogous. At all events it is clear, that further experimental research has here to clear the way.

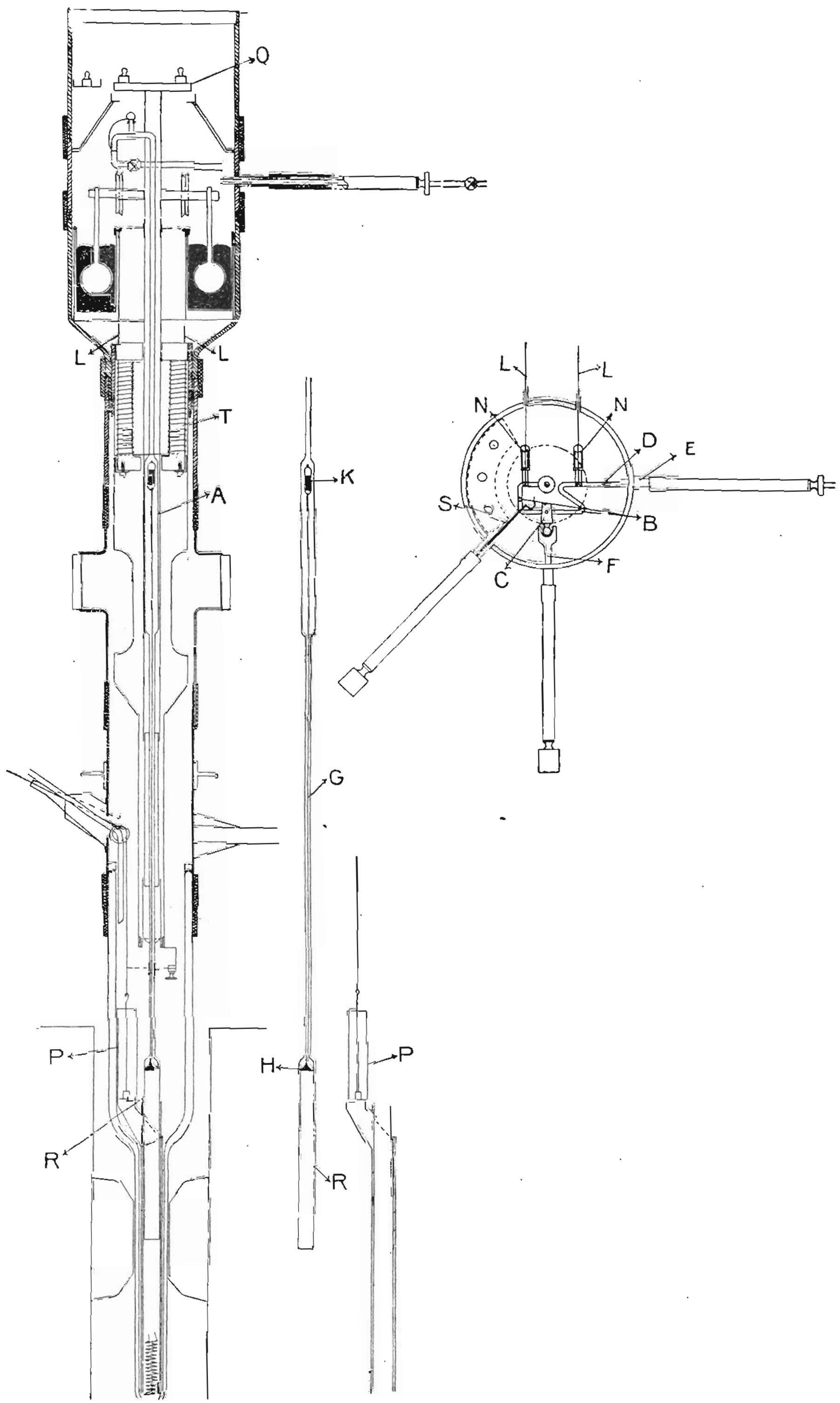
On the one hand the investigation of the properties of different paramagnetic substances at low temperatures, of which every step till now has contributed to gaining a better insight in the problem, has to be continued especially at hydrogen temperatures, to discover, if possible, new phenomena. On the other hand the study of oxygen of which I spoke before is of the greatest importance to elucidate the relation of the negative field to density.

I will therefore dwell some moments on the experimental appliances which made it possible to investigate the properties of mixtures of oxygen and nitrogen.

The method consists in measuring the attraction of a suspended cylinder of which one end is brought between the poles of a powerful Weiss-magnet and the other end reaches outside the field.

The paramagnetic mixture is liquefied in a cylindrical glass tube (Comp. fig. 3) with long capillary suspended in such a way that it floats on mercury. The capillary at its upper end has a glass-stopcock which is used when filling and emptying the cylinder. During the measurements this stopcock is closed. In the tube is an electromagnetic stirrer, a modification of that introduced in the study of mixtures by Kuenen. It is moved by a piece of iron in the upper end of the capillary, under the action of an electromagnet that can be moved up and down.

that in the gas at each temperature there is only one frequency of rotation. Quite recently Keesom has developed a theory in which the distribution of the different frequencies of rotation is taken into account. Calculations by him to compare that theory with experiment have already proceeded very far, and it seems, that on that basis a still better survey of the experimental results can be obtained than with the simple supposition of Einstein and Stern. The formula given by Keesom, when introduced instead of the more simple assumption of Oosterhuis, who worked with a single frequency, gives a good representation also. A criterion between these two representations has not yet been arrived at.



The attraction, which in our first experiments was measured by electromagnetic equilibration (working with a constant field being then necessary), was now, according to a device of Oosterhuis, directly determined by weights placed on a scale at the top of the floated apparatus. All is contained in a hermetically closed space forming one whole with the cryostat, a Dewar-vessel into which liquid nitrogen is poured which is brought into intense circulation by a special pump each time before a measurement.

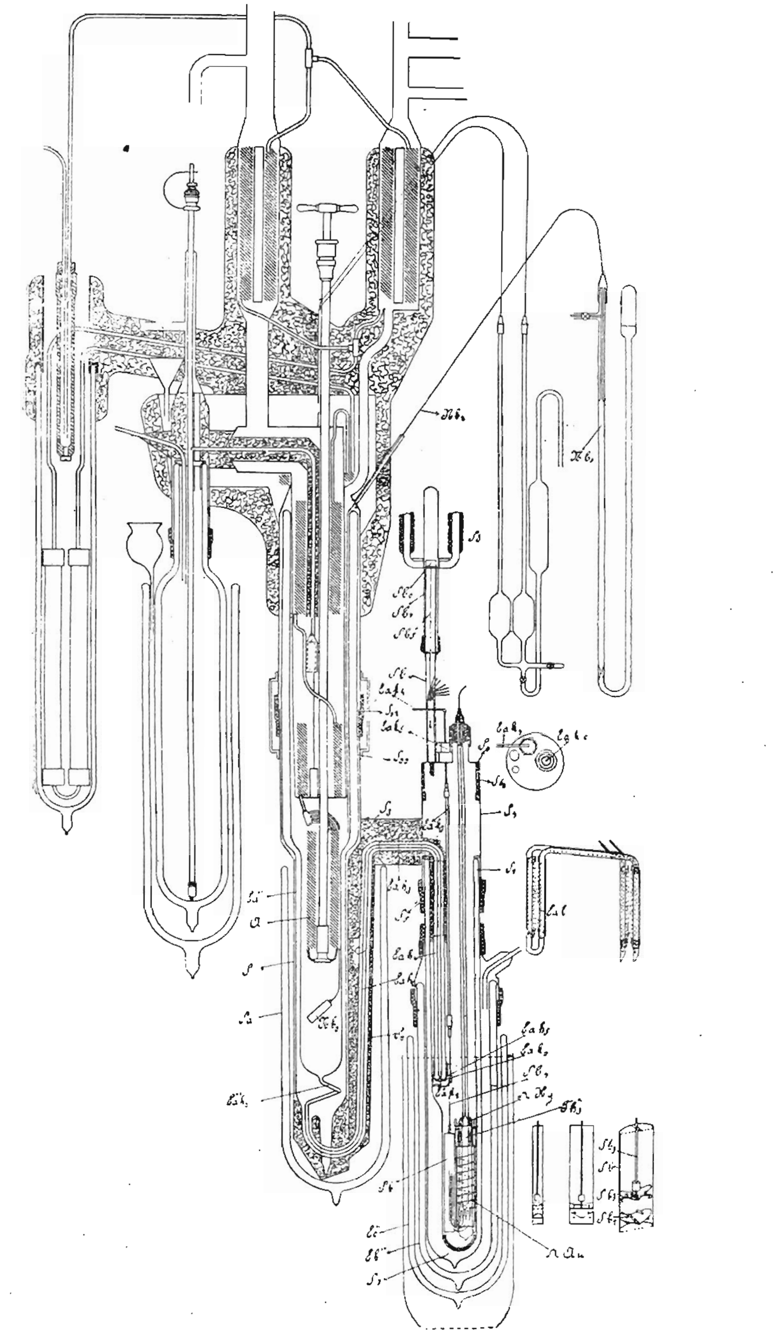
In the cover there is a glass plate through which it is possible to view the putting on the scale of the weights with the aid of a fork manipulated in an india-rubber tube fixed on an opening in the wall of the vessel.

The temperature is regulated by the pressure under which the liquid nitrogen is made to evaporate.

I have yet to explain how the tube is filled. To this end the otherwise freely suspended tube is fixed for a moment; then by moving to and fro an india-rubber tube fixed to an opening in the wall of the apparatus the end of the capillary is connected to the glass tube with greased end which supplies the gas-mixture; when the joint is obtained and proved tight by evacuating the supply-tube, the glass stopcock is opened with the aid of a fork. When the cylinder is filled with the liquefied gas, the stopcock is closed, the capillary disconnected from the supply and the cylinder again freely suspended. The same operations are made when the gas is evaporated from the glass cylinder. By these details it will be evident, that the experiments are rather complicated. But they have marched quite regularly and the research will be continued notwithstanding the complications which are inherent to it in view of the important question of the negative field which it has to decide.

§ 4. **Maximum of density of liquid helium**[1]). Let us now turn to the

[1]) It is a very pleasant duty for me to mention here that I received valuable support to my work from America and to express my best thanks for it to the Welsbach Light Co. and its Director, Mr. Miner, who had the great kindness to collect for me a quantity of helium gas which was obtained from a store of thorianite used in their manufactory.



work with liquid helium. In the first place more accurate determinations have been made of properties pertaining to the thermal equation of state, in particular of the law of vapour tensions, of the densities of liquid and vapour and of the critical pressure and temperature [1]). Of the greatest help in these determinations has been the arrangement of a helium cryostat (fig. 4) [2]).

The principal feature of it is, that liquid helium is transferred from the apparatus, in which it is prepared, to another vessel in which the measuring apparatus can be immersed in the liquid. In the old apparatus the space in which the liquid helium collected was shut off by the liquefying coil; in the new cryostat it has a free and independent exit from above. As I mentioned at Vienna I had then only occasionally succeeded in getting a flowing over into a cryostat vessel of this kind. It is now obtained with perfect certainty and the plant has been arranged so, that the liquefying of helium can go on during the experiments, even when the helium evaporates at reduced pressures, the liquefier and the cryostat being separated by a valve. By the introduction of a stirrer the uniformity of the temperature of the bath is assured, a conditio sine qua non for accurate temperature determinations. — Fig. 4 shows the apparatus connected to the helium-liquefier. The liquid helium gathers, as indicated by a helium thermometer, in the DEWAR-vessel with syphon, at the end of which a valve admits it to the cryostat. The syphon is cooled by a copper capillary through which liquid air is kept flowing; this capillary is wrapped up with the syphon tube in a layer of insulating material; by this means it is ensured, that, when the liquid helium flows over quickly, it takes up but little heat. The stirrer consists of a german silver pump with valved piston and inlet valves in the bottom, the pump is moved electromagnetically, the whole apparatus being, when arranged for experiments, hermetically closed. Only the upper portion of the vacuum-glass is silvered. At the level of the inlet valve the silvering ceases, so that one is able to view the action of the valve and to observe the level of the liquid meniscus in the cryostat-glass.

The cryostat-glass is successively protected by two DEWAR-glasses in which vertical strips are left unsilvered, the first filled with hydrogen, the second with liquid air, this last one is protected by a glass in which circulates alcohol, somewhat warmer than the room. By bestowing all the care usual in precision experiments on the evacuations and other operations and manipulations and by using absolutely pure gases it is possible to have all the glasses perfectly clear, allowing the reading of measuring instruments immersed in the liquid helium during hours.

I will not dwell here on the different particularities in the thermal equation of state of helium. There is a predominance of characteristics the reverse of those of associative substances. The more surprising is the result, that liquid helium has a maximum of density. This is

[1]) Though at this time I will not dwell on the equation of state in general I wish to mention that since the Vienna congress much work has been bestowed, especially by Dr. KEESOM, on the completion of the résumé of the work on the equation of state which has appeared as: Encyklopaedie der mathematischen Wissenschaften, V 10 (Reprinted Leiden Comm. Suppl. n°. 23), and which was alluded to in my Vienna report. This résumé is arranged especially with a view to the law of corresponding states as the expression of similarity and in the second place to the investigations of low temperature, because low temperature research has disclosed causes of dissimilarity which become active on approaching the absolute zero Closely connected with this article is a discussion by KEESOM (Leiden Comm. Suppl. n°. 24, 25, 26) of the second virial coëfficient of monatomic and diatomic gases. The fact that the cohesion of hydrogen, (according to experiments of KAMERLINGH ONNES and BRAAK, Leiden Comm. n°. 101*b*, and of KAMERLINGH ONNES en DE HAAS, [who suggested that the deviation could be related to the change of specific heat] Leiden Comm. n°. 127*c*), does not increase so much at decreasing temperatures, as theory, based on the equipartition principle, requires, is explained by him as due to the influence of temperature according to the quantum theory on molecular rotations, and hence is intimately connected with the decrease of specific heat. I may add that his calculations are based on the assumption of electric doublets in the molecules and that, as from the fact that the relation of MAXWELL between the dielectric constant and refractive index is satisfied for them it follows that hydrogen and similar diatomic gases do not bear an electric doublet, KEESOM has made further calculations on the simplifying assumption that each molecule bears an electric quadruplet. He then gets for the higher temperatures results quite similar to those for doublets, for the lower temperatures the calculations are not yet finished, but he thinks the conclusion referred to above will not be altered.

[2]) Leiden Comm. n°. 123.

found at 2.°2 K. It is most probable, that the helium atom has an invariable volume and we would believe it a hard, smooth sphere; in this case an increase of the volume of the liquid helium at lower temperatures is even more curious than it would be otherwise. I came to suppose that one part of the molecular attraction, more local and of smaller range than the other part of comparatively large sphere of action, diminishes with temperature and has for helium at 2°.2 K. wholly withdrawn within the space occupied by the atom. In seeking possible causes it seemed to me, that the properties of PLANCK vibrators were intervening and that the quantum theory had to be applied to the theory of molecular attraction on coming near to the absolute zero. PLANCK at that time had not yet introduced the idea of zero-point energy, which we have mentioned before.

It seemed beyond question that the kinetic energy of the progressive motion was proportional to temperature. At present one might look upon the maximum of density as a proof that a zero energy has to be accepted for the zigzag motions of the molecules of liquid helium in their heat agitation, which KEESOM's calculations show to be the case for gaseous helium [1]). If one applies the theory of VAN DER WAALS with constant molecular cohesion and incompressible, non associative molecules, then, when the kinetic energy tends with decreasing temperature at a certain value of temperature to a practically constant value, the density is found to assume a maximum value at this temperature and remain constant at lower temperatures. The experiments give an increase of the volume, when the liquid helium was cooled under 2.°2 K, but the experiments have been made with a less perfect cryostat than the one I have described before and, though they seemed conclusive, it will be well to repeat them.

At all events the fact of maximum density of such a simple substance as helium, the simplest of all, as we think, seems a fundamental one for the theory of the equation of state. The further experimental study of it (including the investigation of related properties such as viscosity, capillarity, specific heat, refraction index and dielectric constant) is therefore very important.

[1]) The idea of zero-point energy has received a valuable confirmation by different interesting papers of KEESOM. In one of them (Leiden Comm. Suppl. n⁰. 30*a*) are given the motives for the application of the quantum theory to the molecular translation and it is shown that the introduction of zero-point energy gives results which are not contradicted by experimental data, which is the case if the zero-point energy is omitted.

§ 5. **Superconductors**. It was also with the aid of the new helium cryostat that I discovered the extraordinary behaviour of the electric resistance of some metals at the lowest temperatures.

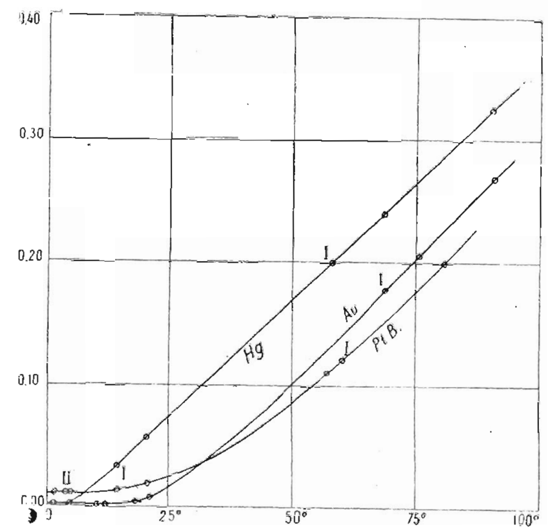


Fig. 5.

The variation of the resistance of metals with the temperatures has been a subject of research in the Leyden laboratory for many years. It seemed first impossible to me that the resistance of pure metals (gold, platinum, silver) would continue to decrease at low temperatures according to the approximately linear law, which prevails between the ordinary temperature and that of liquid air, (compare fig. 5). This would lead to a negative resistance at absolute zero, which has no meaning or to the vanishing of the resistance at a temperature above the absolute zero, which, though now found to be the case, seemed then inadmissible, because it was without any analogy at that time. In the mean time came DEWAR's great achievement of making measurements in liquid hydrogen and his fundamental result that at temperatures as low as those of liquid hydrogen the diminution of resistance with temperature decreases considerably. The supposition was now allowable, that the electrical resistance would only vanish at the absolute zero. A closer investigation of the variation of the resistance with the temperature, undertaken by M. CLAY and myself, was directed by the conception of the electronic theory. The conduction of electricity through metals is according to this theory brought about by the free electrons moving through the space occupied by the metal as if they were molecules of a gas or a vapour. In this movement they come into collision with the atoms and at the impact give off current-energy. The resistance against the migration of the free electrons under the influence of the electromotive force increases with the velocity of the heat-agitation of these electrons and is proportional to the number of free electrons per unit of volume and to the free path of an electron between two impacts with an atom. If we suppose, that the heat movement of the free electrons is regulated by temperature in the same way as that of gas-molecules and that the density of the electronic gas and the free path of the electrons are constant, we find that the conductivity will increase with decreasing temperature.

If we suppose, that at lower temperatures the density of the electronic vapour around the atoms diminishes, the electronic gas having become by the cooling an electronic vapour, the conductivity will on the contrary diminish by this cause. It can therefore reach a maximum at a very low temperature and then, the temperature continuing to decrease, continue to decrease to an infinitely small value at the absolute zero, all electronic vapour being then frozen to the atoms. The metal would then as KELVIN supposed have turned into an insulator. For a long time we were confirmed in this idea by the accumulating results of experiments. It was curious though, that the temperature at which we might suppose the resistance to become proportional to absolute temperature appeared to become lower, the purer the metal was, that we could obtain. Of course there could be no question of finding a minimum of resistance by

cooling before this proportionality point was in view. I already inclined to the idea, that had been expressed by DEWAR, that resistance would tend to vanish at the absolute zero itself, when the experiments with liquid helium in December 1911 brought quite a revelation.

The resistance of very pure platinum became constant instead of passing through a minimum or of tending to vanish at the absolute zero. This constant value could be ascribed to impurities. In the research by CLAY and me it had been found that very small quantities of these give a relatively considerable additive mixture-resistance which is approximately independent of temperature.

Allowing a correction for this additive resistance I came to the conclusion that probably the resistance of absolutely pure platinum would have vanished at the boiling point of helium (comp fig. 6 and 7). Gold behaved in the same way as platinum. At helium temperature there remained a resistance independent of temperature, which could again be interpreted as an additive mixture-resistance.

According to the probable result, that pure metals would show a

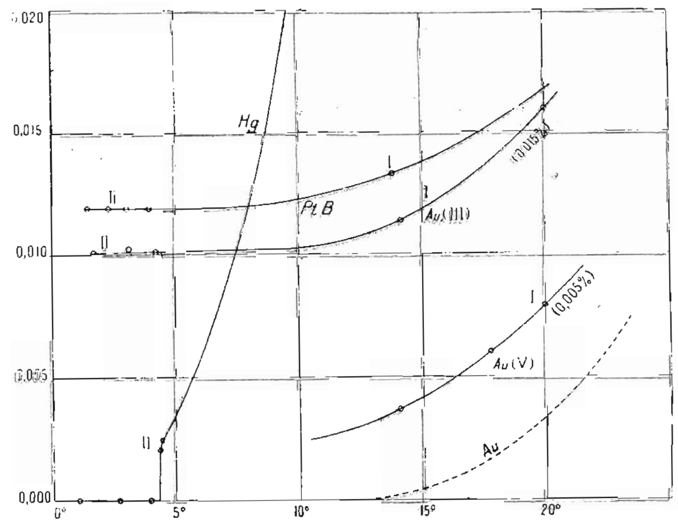


Fig. 6.

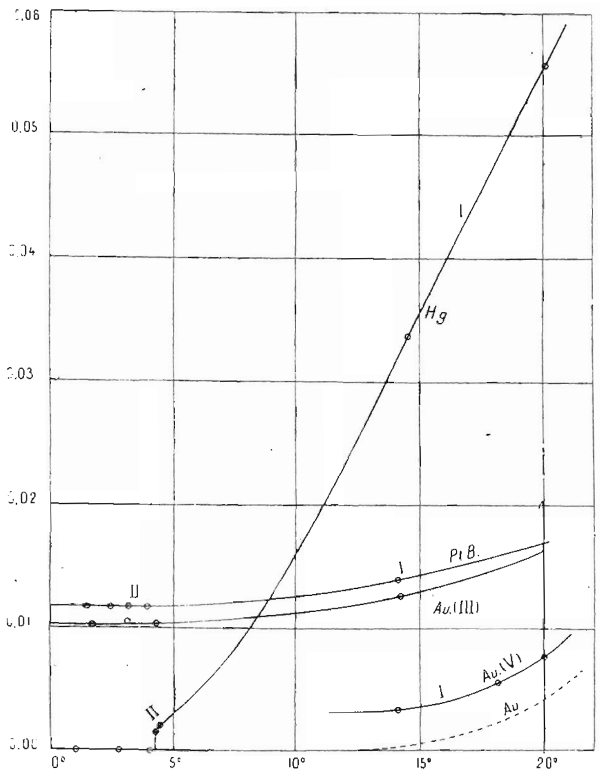


Fig. 7.

practically infinite conductivity, the view formed of electric conduction had to undergo a fundamental change. It is not the free electrons that freeze to the metal: on the contrary it is the impediments which the atoms oppose to the rectilinear motion of the free electrons and which limit the free path, which lose their extension.

PLANCK in the quantum theory of radiation had introduced vibrators of which the mean energy vanishes at a temperature distinctly above the absolute zero and EINSTEIN had established the new theory of specific heat, which considers the heat-agitation of solids as the oscillations of these vibrators. If we accept that the impediments to the movement of the free electrons through the metal depend on the amplitude of these vibrators, then we get a simple

view of the variation of the electric resistance with the temperature and the practical vanishing of it, when the vibrators are frozen, is explained [1]).

The theory of the electric resistance joining hands in this way with the kinetic theory of the solid state on electrodynamical basis, it became of even greater interest to realise the superconductive state, the existence of which had only become probable by the experiments with platinum and gold. Experiments having been frustrated by traces of impurities so extremely small as were found, using the purest gold of any mint of the world, there was only one metal which one could hope to get into wires of a higher state of purity, viz. mercury. The temperature at which the mean energy of a vibrator vanishes depends according to PLANCK on its frequency. This frequency determines a certain temperature and at $^1/_{10}$ of this temperature we can put the energy practically zero. By deducing the frequency of the mercury vibrators from the law of corresponding states as applied to metals, it could be foretold, that the resistance of a wire of solid mercury would be measurable

[1]) WIEN (Berl. Sitz. Ber. Jan. 16, 1913 p. 184) has elaborated the idea, that the resistance depends on the energy of PLANCK-vibrators in a way that shows clearly the deficiencies in the reasoning which guided me in foretelling the vanishing of the resistance of mercury.

From quite another point of view KEESOM has applied recently the quantum theory to the electric phenomena in metals. He showed that, by the application of the quantum theory with the assumption of zero-point energy to the free electrons considered as a monatomic gas, most of the difficulties which till now were inherent to the theory of free electrons in metals (small specific heat of electrons, not freezing of electrons to the molecules at the lowest temperatures) disappear and that in that way one coherent scheme can be drawn up in which the field of high temperatures investigated by RICHARDSON on the one hand, and that of low temperatures where the assumption of WIEN as to constant number and velocity of the electrons holds on the other receive their proper place. He applied this theory to the reversible thermo-electric phenomena and derived limiting laws for low temperature for them. His conclusion as to the way in which thermopower decreases with temperature approaching to 0° K., which conclusion specifies the conclusion drawn by NERNST from the recent general formulation of his heat theorem, completely agrees with not yet published results of observations on the thermoelectric forces of different combinations of metals down to the temperatures of liquid helium by KAMERLINGH ONNES and HOLST.

at the boiling point of helium, but would fall to inappreciable values at the lowest temperatures which I could reach.

With this beautiful prospect before me there was no more question of reckoning with difficulties. They were overcome and the result of the experiments was as convincing as could be hoped (fig. 8).

No doubt was left of the existence of a new state of mercury in which its resistance has practically vanished.

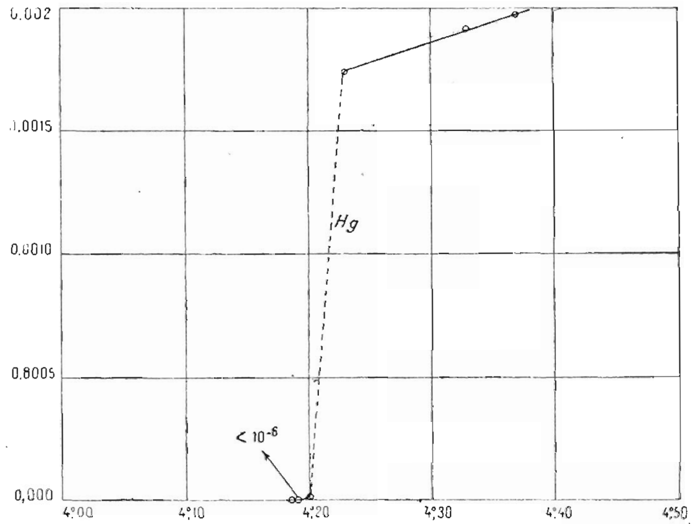


Fig. 8.

I will pause a moment at the experimental arrangements [1]). With regard to the problem of refrigerating the resistance I have mentioned, that it was solved by the establishment of the new helium cryostat (comp. § 4 and fig. 9). I will now no longer dwell on this part of the problem and turn to the description of the wires the resistance of which was measured The wires of solid mercury needed to be very fine to leave at the low temperature a resistance great enough to be measured with precision. They are obtained by freezing mercury in very narrow capillaries. Mercury was distilled

[1]) Leiden, Comm. n°. 124*c*.

repeatedly in vacuo at low temperatures using liquid air for condensing it, and filled in vacuo into the capillaries. The capillaries (comp. fig. 10, 11) have the form of a U tube as long as the height of the column of liquid helium in the cryostat allows. At the top of each arm there is a wider tube, a dilatation head, for taking up the mercury that enters or leaves the capillary when the mercury is frozen or thawed; care is always taken that in these operations the temperature remains lowest at the bottom. Even with this precaution it is difficult to prevent cracking by melting or breaking of the continuity of the wire in freezing. But good wires of $^1/_{20}$ mm. diameter and 20 cms. length, having say 100 ohms of resistance at 0° C. could be regularly obtained. Greater resistances are made by soldering together in series a number of U tubes with dilatation heads.

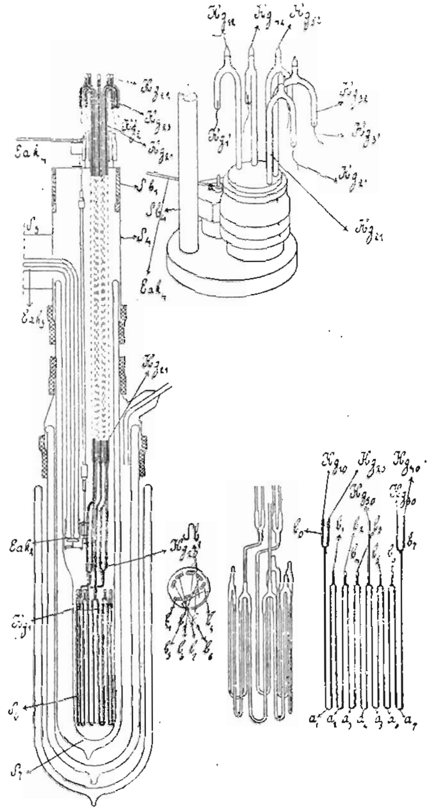


Fig. 9.

To each of the ends of the series of U tubes two tubes are fastened filled with mercury, one of them conveying the current through the wire, the other making the connection to the potentiometer. (Comp. fig. 9). This is the theoretically simplest form, a ramification entirely of the same metal. In another form the potentiometer wires consist only for a small length of solid mercury, platinum being sealed into the tubes, which is again soldered to the copper wires leading to the measuring apparatus (Comp. fig. 10 and 11).

I have already said that the result of the experiment left no doubt about the disappearance of the resistance of mercury. Cooling the resistance to 4.°2 K., somewhat below the boiling point of helium, it had become 500 times less than that of the solid wire at the

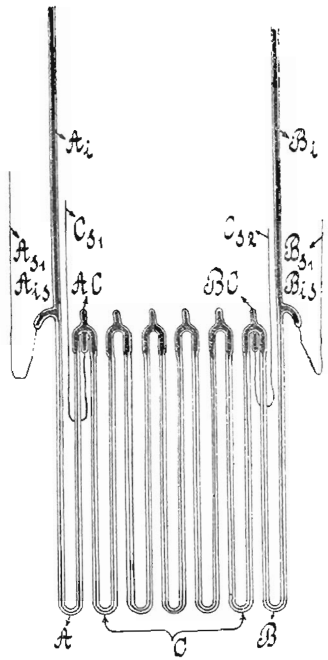


Fig. 10.

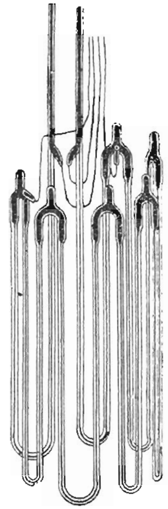


Fig. 11.

melting point of mercury. At this point within some hundredths of a degree came a sudden fall, not foreseen by the vibrator theory of resistance that I had framed, bringing the resistance at once to less than a millionth of its original value at the melting point and a thousand millionth of it at the lowest temperatures obtained.

Mercury has passed into a new state, which on account of its extraordinary electrical properties may be called the superconductive state. There is left little doubt, that, if gold and platinum could be obtained absolutely pure, they would also pass into the superconductive state at helium temperatures. The behaviour of metals in this state gives rise to new fundamental questions as to the mechanism of electrical conductivity.

It is therefore of great importance that tin and lead were found to become superconductive also. Tin has its step-down point at 3°.8 K., a somewhat lower temperature than that of the vanishing point of mercury. The vanishing point of lead may be put at 6° K. Tin and lead being easily workable metals, we can now contemplate all kinds of electrical experiments with apparatus without resistance. A much wider field is opened for the investigation of the properties of the superconductive state than would be accessible with mercury.

The extraordinary character of this state can be well elucidated by its bearing on the problem of producing intense magnetic fields with the aid of coils without iron cores. — Theoretically it will be possible to obtain a field as intense as we wish by arranging a sufficient number of ampèrewindings round the space where the field has to be established. This is the idea of Perrin, who made the suggestion of a field of 100 000 gauss being produced over a fairly large space in this way. He pointed out that by cooling the coil by liquid air the resistance of the coil and therefore the electric work to maintain the field could be diminished. Fabry has studied what would be the best construction of coils for producing intense fields assuming that the Joule heat can be withdrawn at the same rate at which it is generated, and has calculated the electric work required under these conditions. He finds that the energy absorbed in such a coil in watts is proportional to the linear dimensions of the coil, and to the specific resistance of the metal. In order to get a field of 100 000 gauss in a coil with an internal space of 1 cm. radius, with copper as metal, and cooled by liquid air 100 kilowatt would be necessary (assuming that the coil has been constructed in the way which is most advantageous from an electric point of view, abstracting from the question of cooling). The electric supply, as Fabry remarks, would give no real difficulty, but it would arise from the development of Joule-heat in the small volume of the coil the dimensions of which are measured by centimetres, to the amount of 25 kilogramme-calories per second, which in order to be carried off by evaporation of liquid air would require about 0.4 litre of liquid air per second, let us say about 1500 litres of liquid air per hour. We may add to Fabry's objection, that the preparation of 1 litre of liquid air per hour is at present reckoned as requiring not much less than $^1/_2$ KW. According to this standard 7 times as much work would be necessary for the cooling than for the current. By a judicious use of the cold of the vapours this number can be reduced, but the proportion will remain unfavourable.

But the greatest difficulty, as FABRY points out, resides in the impossibility of making the small coil give off the relatively enormous quantity of JOULE-heat to the liquefied gas. The dimensions of the coil to make the cooling possible must be much larger, by which at the same time the electric work and the amount of liquefied gas required becomes greater in the same proportion. The cost of carrying out PERRIN's plan even with liquid air might be about comparable to that of building a cruiser.

We should not advance much by cooling with liquid hydrogen. Calculating in the same way as before for a coil of 1 cm. radius, we arrive with silver at a more favourable figure as regards the number of litres of liquid hydrogen, this being 700 per hour, but the ratio of cooling work and electric work, when in the same way as before the preparation of a litre of liquid hydrogen is put at 1 $^1/_2$ K. W., is found even more unfavourable, and it seems not probable that it can be turned into a favourable one even when considerable economies are realized.

The figure for liquid hydrogen moreover would again on the ground mentioned have to be considerably increased, if the question of the possibility of drawing off the heat is considered, and we should arrive at a fantastic extension of the Leiden plant, if we wished to supply the quantity of liquid hydrogen that would be wanted.

We should no more get a solution by cooling with liquid helium as long as the coil does not become superconductive.

The problem which seems hopeless in this way enters a quite new phase when a superconductive wire can be used. JOULE-heat comes no more into play, not even at very high current densities, and an exeedingly great number of ampèrewindings can be located in a very small space without in such a coil heat being

developed. A current of 1000 amp./mm². density was sent through a mercury wire, and of 560 amp./mm². density through a lead wire, without appreciable heat being developed in either. Even when currents of these densities pass through the sufficiently cooled superconductor there is no appreciable JOULE-heat to withdraw, we have only to prevent heat being conveyed by radiation or conduction to the superconductor, by which it would be warmed to the step-up point of resistance and become an ordinary conductor.

There remains of course the possibility that a resistance is developed in the superconductor by the magnetic field. If this were the case, the JOULE-heat depending on this resistance would have to be withdrawn. One of the first things to be investigated as soon as the appliances, which are arranged for making the projected researches on magnetism at helium-temperatures will be ready, will be this magnetic resistance [1]). We shall see that it plays no role for fields below say 1000 gauss.

Having succeeded as mentioned in sending a current of 8 amperes through a lead wire of $^1/_{70}$ mm². diameter without appreciable JOULE-heat being developed in it, a coil was wound of this wire, where 1000 windings found a place on a length of 1 cm. in a layer of 1 cm.

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[1]) The experiments on the question if the magnetic field develops resistance in superconductors, to which we alluded above have been made in the mean time. They have given a startling result (see Comm. No. 139*f*). In fields below a threshold value (say 600 gauss for lead at the boiling point of helium) there is developed no resistance at all by the field. In fields above that threshold value a relatively considerable resistance is developed, which increases with the field.

Of course the now acquired knowledge of this property completely changes our view on the problem of obtaining intense magnetic fields with coils of superconductive material.

The text was written in the idea founded on analogies that the magnetic resistance would increase in a continuous way with the field. Starting from what was observed with our small coil and even accepting an increase with the square of the field it seemed probable that the magnetic resistance would not yet come seriously into account with a field of 100.000 gauss.

An unforeseen difficulty is now found in our way, but this is well counterbalanced by the discovery of the curious property which is the cause of it.

The insulation of the wire was obtained by putting silk between the windings, which being soaked by the liquid helium brought the windings as much as possible into contact with the bath. The coil proved to bear a current of 0,8 ampere without losing its superconductivity. There may have been bad places in the wire, where heat was developed which could not be withdrawn and which locally warmed the wire above the vanishing point of resistance. That magneto-JOULE heat came into consideration is not probable, because no appreciable resistance was found below the threshold value of current at which resistance became measurable.

I think it will be possible to come to a higher current density approaching the threshold value at which resistance appears with a stretched wire of the same kind and section, if we secure a better heat conduction from the bad places in the wire to the liquid helium by interposing, instead of silk, foil of a non-superconductive metal between the windings. An ordinary metal in comparison with a superconductor acts as an insulator; in a coil of bare lead wire wound on a copper tube the current will take its way, when the whole is cooled to 1°.5 K, practically exclusively through the windings of the superconductor. If the projected contrivance succeeds and the current through the coil can be brought to 8 amperes as for the stretched wire, we shall approach to a field of 10000 gauss. The solution of the problem of obtaining a field of 100000 gauss could then be obtained by a coil of say 30 centimeters in diameter and the cooling with helium would require a plant which could be realised at Leiden with a relatively modest financial support. If we cannot wind the wires so closely as was done in the experiment which I have described, the dimensions of the coil of which I have spoken will have to be taken greater and of course the difficulties and cost will increase proportionally. When all outstanding questions will have been studied and all difficulties overcome, the miniature coil referred to may prove to be the prototype of magnetic coils without iron, by which in future much stronger and at the same time much more extensive fields may be realized then are at present reached in the interferrum of the strongest electromagnets. As we may trust in an accelerated development of experimental science this future ought not to be far away.

I want now to consider a side of the problem that I have not touched upon yet. All that has been said about superconductors holds only for currents below a certain threshold value of density. At the end of the superconductive wire there is no potential difference as long as the current remains below the threshold value for this wire As soon as this value is surpassed, potential differences originate and the wire by a process that is not quite cleared up obtains ordinary resistance. [1]) By the enormous increase of resistance a considerable heating can then take place. As an example I can quote, that a wire of superconductive mercury in a capillary immersed in liquid helium bearing a current of 1000 amp./mm.^{2} density warmed itself to a temperature above the boiling point of hydrogen, another example is a wire of bare lead cooled in liquid helium remaining superconductive with a current of 420 density, which on raising the current density to 940 was melted. It is very probable that one place of the wire had been heated to a temperature above the vanishing point and assumed ordinary resistance: all the tension being concentrated on that part, the JOULE-heat could not be sufficiently withdrawn, the forming of a bubble of gaseous helium and heating of the lead to the melting point followed immediately.

If matters are scrutinized more closely it seems that generally, when the current surpasses the threshold value, a local heating of a very small portion of the superconductive wire takes place, so that the step-up point of resistance is reached; at greater densities this temperature spreads over the wire, till there is equilibrium between the heat given off and the JOULE-heat generated. I cannot go into all the details of the phenomena, but the bearing upon the question of experiments with superconductors as soon as we go to great current densities is evident. The great question is, whether we have to do with phenomena that are to be attributed to local disturbances by bad places, places at which JOULE-heat or PELTIER-heat is developed, or

[1]) Leiden Comm. n°. 133.

that they will occur at a given current density in the metal itself even if it is homogeneous, unstrained, everywhere crystallized in the same manner.

If the potential-phenomena in superconductors charged above the threshold-value of current density depend on local disturbances by bad places, we must conclude that the higher limit for microresidual resistance which we deduce from this threshold value is also to be ascribed to bad places. We are then led to the conception that conductivity in the superconductive state itself is yet many times greater than it has already been found to be i. e. equal to 10^9 times that at ordinary temperature, so that it may be put practically infinite

Let me again make clear the conclusions by applying them to the problem of producing intense magnetic fields by coils without iron. We may be sure that by continuing the investigation we shall find the means of preparing wires free from bad places. There would then be no limit to the current density at all and the magneto Joule-heat would become the determining factor for the dimensions and the intensity of the field.

If we take the other view of the potential phenomena in superconductors and assume that they are inherent to pure metals, then it will not be possible to go under a certain limit of current density and we shall probably not be able to construct the magnet on such a very small scale as we deduced before. But against that may be put, that we should be sure of the existence of quite a new world of electrical phenomena in conductors. The first remarkable thing in this new domain would be electrical conduction of metals not obeying Ohm's law.

It is not difficult to frame hypothetical explanations for this on the lines of the explanation given for the mechanism of ordinary resistance. We have to remember that according to our supposition the vibrators which cause the resistance in ordinary conductors have come to rest in superconductors though they are surrounded by free electrons in heat agitation. It means that, when free electrons in heat movement come near the vibrators, they pass by without coming into collision and giving off energy. The energy of the vibrators remains infinitely

small. But if a sufficient migrative movement is impressed on the free electrons in addition to their heat agitation there can occur collisions in which the electrons can give off energy to the vibrators. The more the temperature at which the experiment is made differs from the temperature of the vanishing point, the greater must be the migration movement to be added to the heat movement in order that absorption of energy by the vibrators will be brought about. As soon as the vibrator oscillates, the free electrons which come in the neighbourhood are stopped in their motion i.e. a potential difference is required to force the current through the wire. This hypothetical explanation may be quoted here to show that the superconductive state raises questions of fundamental interest for the theory of quanta, which in the last three years has taken a prominent place in very different departments of physics.

If we make ourselves free from accepted theoretical ideas, we can draw attention to the analogy with the generation of waves on water when the velocity of the wind exceeds a certain value. There is perhaps even a deeper ground in this analogy pertaining to the question of stability of motion.

At all events, if the potential phenomena are not due to disturbances which we can eliminate, they are of an interest that will repay us for the difficulties they might give, when we wish to produce an intense magnetic field by a superconductive coil.

If we return now to the simpler case of superconductors not overcharged with current densities above the threshold value, it gives rise to highly interesting questions also.

When we calculate on the basis of the electron-theory the mean free path of the free electrons in superconductors at the lowest temperatures, we find, instead of the values of the order of the dimensions of molecules that hold at ordinary temperature, values of the order of a meter.

Would then a block of superconducting metal behave like a Röntgen tube for electrons projected with a certain velocity? And will a superconductive film be traversed more easily or with less deviation from their path by all kinds of electric rays? Professor Lenard and

I have put ourselves this question and we hope before long to make experiments in this direction.

An other question was the following. If electrons can pass from a superconductor into a metal with ordinary resistance and return from that metal in the superconductor, will they sustain a loss of energy and will a resistance by contact arise in the superconductor? A thin layer of tin obtained by tinning over a wire of constantan became superconductive notwithstanding the contact with the ordinary conductor. It is true that the current density in the experiment was very small and continuation of the experiments is therefore desirable. But in any case the preliminary result seems very difficult to explain with the ordinary conception of the movement of the electrons.

Recapitulating what we said about the superconductive state we may conclude, that the continuation of the investigation of it promises to throw light on different questions of great interest.

At the next International Congress of Refrigeration I hope to be able to report on some further results of this study.