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Investigations into the properties of substances at low temperatures, which have led, amongst other things, to the preparation of liquid helium

Nobel Lecture, December 11, 1913

Since you have done me the honour of describing to you my investigations into the properties of substances at low temperatures, which have also led me, amongst other things, to the preparation of liquid helium, I must first of all express my deepest thanks to your old and famous Academy for distinguishing me in this manner. This has happened at a time when the continuation of my work will make great demands upon me. Nothing could make me more able than your good will does to meet new problems with the same hopeful confidence with which, 30 years ago, I met difficulties now overcome.

The main aim in investigations at low temperatures has greatly changed since then. When I first turned to this field of work the aim was still to liquefy statically the gases which up to then had not been mastered and to pour into open containers those gases which it is most difficult to liquefy.

What has given a character of its own to the Leyden work from the very beginning is that I allowed myself to be led by Van der Waals' theories, particularly by the law of corresponding states which at that time had just been deduced by Van der Waals.

This law had a particular attraction for me because I thought to find the basis for it in the stationary mechanical similarity of substances and from this point of view the study of deviations in substances of simple chemical structure with low critical temperatures seemed particularly important.

I was greatly drawn to making the necessary precision measurements at low temperatures. To this end large measuring instruments had to be maintained at constant temperatures, and one had also to construct suitable temperature baths - which would also be very useful for other investigations - to cover the whole field of low temperatures.

Just as I was thinking about how to do this, the basic classic work of Wroblewski and Olszewski appeared on the static liquefaction of oxygen. This meant that the determination of isotherms of hydrogen in a bath of

liquid oxygen was of great value, particularly with regard to liquefaction of hydrogen. These determinations were not carried out until the second ten-year period of the cryogenic institute and the results could not be published until many years after Dewar had already liquefied hydrogen. The first great stage in the development of the cryogenic laboratory, which made measurements in a bath of liquid oxygen possible, was likewise not reached until after ten years. Olszewski and Dewar had by then already solved the problem of pouring oxygen into open containers.

The Leyden process differed from the others as follows : in order to have a permanent bath available, the evaporated oxygen was liquefied again and conducted through a closed circulation system. When the apparatus in the Leyden laboratory was further developed the production of circulation systems of the same type was considered, although the investigations to be carried out were directed towards still lower temperatures. Earlier experience could thus be used in attacking a later problem and this was decisive for the liquefaction of helium. Thus the whole cryogenic laboratory still bears the marks left on it by its early problems.

The range of low temperatures now available to us far exceeds what I ever dreamt of at the beginning, for helium was not discovered until later and this allows us to get five to ten times nearer to absolute zero than is possible with hydrogen.

At the same time the aim of the cryogenic laboratory, which had originally been a limited one, became much more diverse.

This was the case as early as ten years ago, when I discussed in my rectorial address the programme of the laboratory at that time. Besides thermodynamic questions, questions relating to other fields were dealt with.

Thermodynamic problems were then in the forefront as far as the cryogenic section of the laboratory was concerned, because it was particularly work on the equation of state which was concentrated on low temperatures. But questions of other types, which demanded investigations at low temperatures, had become so numerous and important that I had felt it indicated that I should continue the other groups of work also exclusively at low temperatures, and dedicate the Leyden institute entirely to a study of the general character of the influence of low temperatures.

It is due to having specialized in this way that I was able to co-operate with a number of learned men who accepted the hospitality of the laboratory. The decision to make the Leyden institute an institute which co-operated with other larger ones, being a special institute for the more difficult

work in the field of low temperatures, has been found to be well worth as the scientific basis of this collaboration.

During the specialization in the Leyden institute, which is now completed, I was of course convinced that the investigations into the properties of substances at low temperatures would provide explanations for many of these properties. But my expectations were far surpassed by the reality. Not only has it been generally desirable - and to a far greater extent than was foreseen - to simplify as far as possible the conditions under which the phenomena occur, via extensive suppression of thermal motion, but it has also been shown that with liquid helium one can take an unexpectedly long step in this direction, as it permits temperatures to be reached which, for certain phenomena, represent practically absolute zero. Further discoveries in another field have made necessary, in an unexpected connection, the examination of many properties in the neighbourhood of absolute zero. The Nernst heat theorem and, especially, Planck's quantum theory and zero-point energy theory have made measurements at low temperatures of prime interest to physicists.

It is true that Faraday's problem as to whether all gases can be liquefied has been solved step by step in the sense of Van der Waals' words "matter will always show attraction", and thus a fundamental problem has been removed. At the same time, however, the question asked by Planck introduces a problem which is probably no less fundamental, to the solution of which investigations into the properties of substances at low temperatures can contribute.

I would now ask you to follow me into the Leyden laboratory.

As I have already briefly explained, the measurements are made in baths of liquid gases, which are maintained as long as is required in cryostats (equipment for maintaining constant low temperatures), the evaporated gas being allowed to circulate - it is sucked up and liquefied again.

The cycles for the various gases, as in Pictet's famous experiment, are joined in cascades, so that the cold bath, which can be maintained by a previous cycle, also serves to liquefy at a lower temperature the gas which circulates in the following cycle. In Fig. 1 is shown diagrammatically the various cycles with the exception of that for helium. They are shown by various sorts of lines.

The first cycle contains methyl chloride. The liquid methyl chloride is in a condenser cooled by water. From the condenser it passes into a refrigerator, where it evaporates under a pressure corresponding to the temperature necessary to liquefy ethylene. The vapour is sucked up by a large vacuum pump
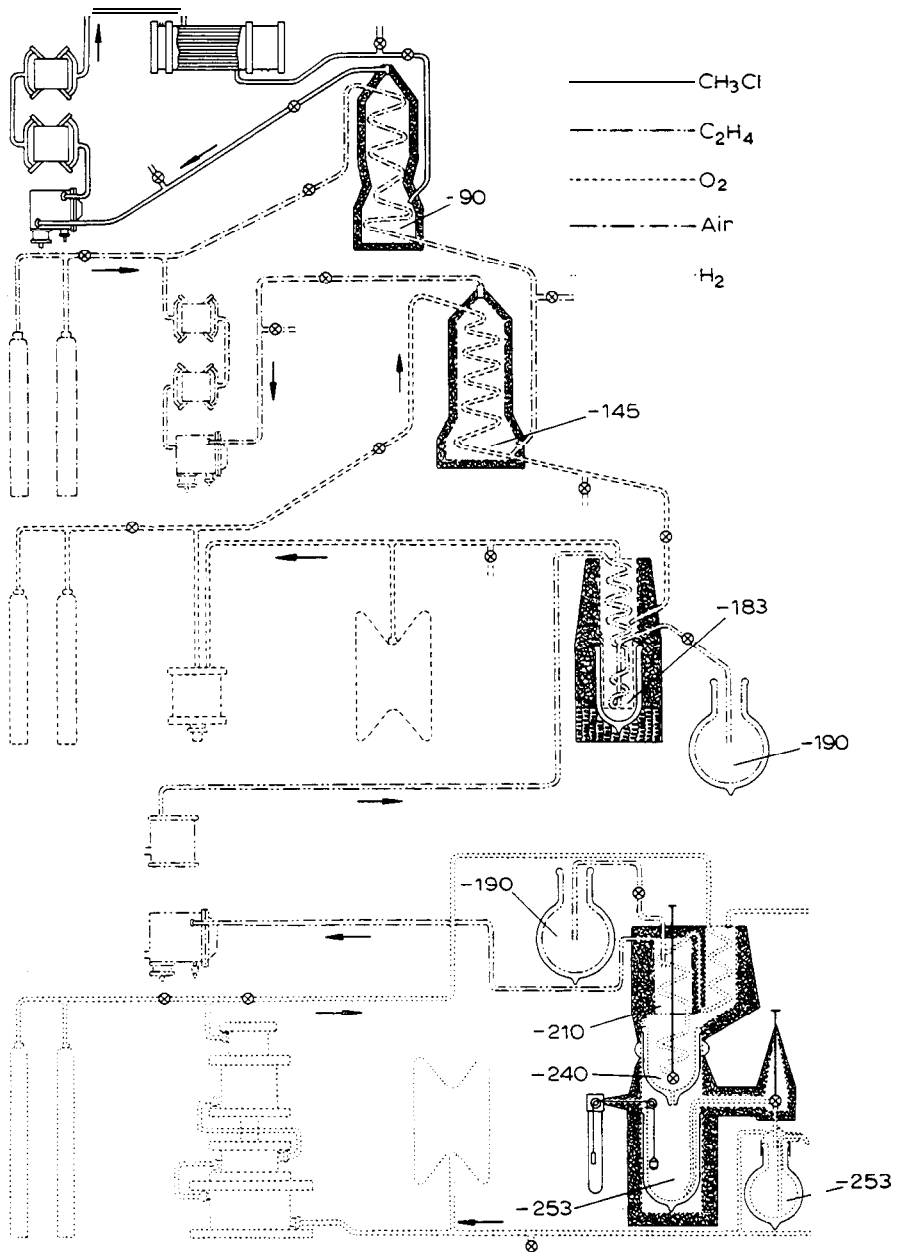
Fig. 1.

through a regenerator (in which, according to the counter-current principle, it flows past the ethylene which is being cooled), and is led by a conjugated compressor back to the condenser where it is liquefied.

In the second cycle is the ethylene. Circulation proceeds in the same way as in the first cycle.

In the third cycle the oxygen circulates in the same way. The liquefied oxygen can also serve to produce liquid air in the oxygen refrigerator.

The cryostat with the bath of liquid oxygen, of which I spoke before, was erected without using vacuum glass vessels. It was connected to the liquefying apparatus and the measurements could thus only be made in the immediate neighbourhood of this apparatus. Dewar revolutionized working at low temperatures by introducing his silvered vacuum glass vessels. The liquid oxygen could be stored in these vessels and transported in them from the liquefying apparatus to the point where one wished to use it. When working the cycles and in my subsequent work I found Dewar's ingenious idea very useful.

The liquid air is prepared in the fourth cycle. The other cycles are closed but this can be broken into. Air is sucked up from the room and a supply of liquid air can be stored in open vacuum glass vessels.

Shortly after success had been achieved in making available a permanent bath of liquid oxygen, the great master of refrigeration technique, Linde, discovered the process by means of which he created the liquid-air industry. This ingenious discovery permits the air, starting from normal temperature, to be liquefied without intermediate stages. You will see that the preparation of liquid hydrogen and liquid helium in the following cycles, which demands each time a similarly large temperature drop without an intermediate stage, is based on the principles of the Linde process. We, however, still always prepare the liquid air by means of cycles joined in cascade, as already described. When considering this arrangement, which is also very economical and supplies about 14 litres per hour, it must be borne in mind that all the relevant cycles here must be ready for continuous work so that during experiments in the laboratory the whole temperature range down to -217°C is always freely available.

Fig. 2 shows a view of the four first cycles of the Leyden cascade. The conjugated pumps for the methyl chloride and ethylene circulation systems and the Brotherhood compressor for the oxygen cycle can clearly be seen. (Many pieces of equipment can also be seen which are used for taking various measurements; the figure does not show either the Brotherhood air compressor
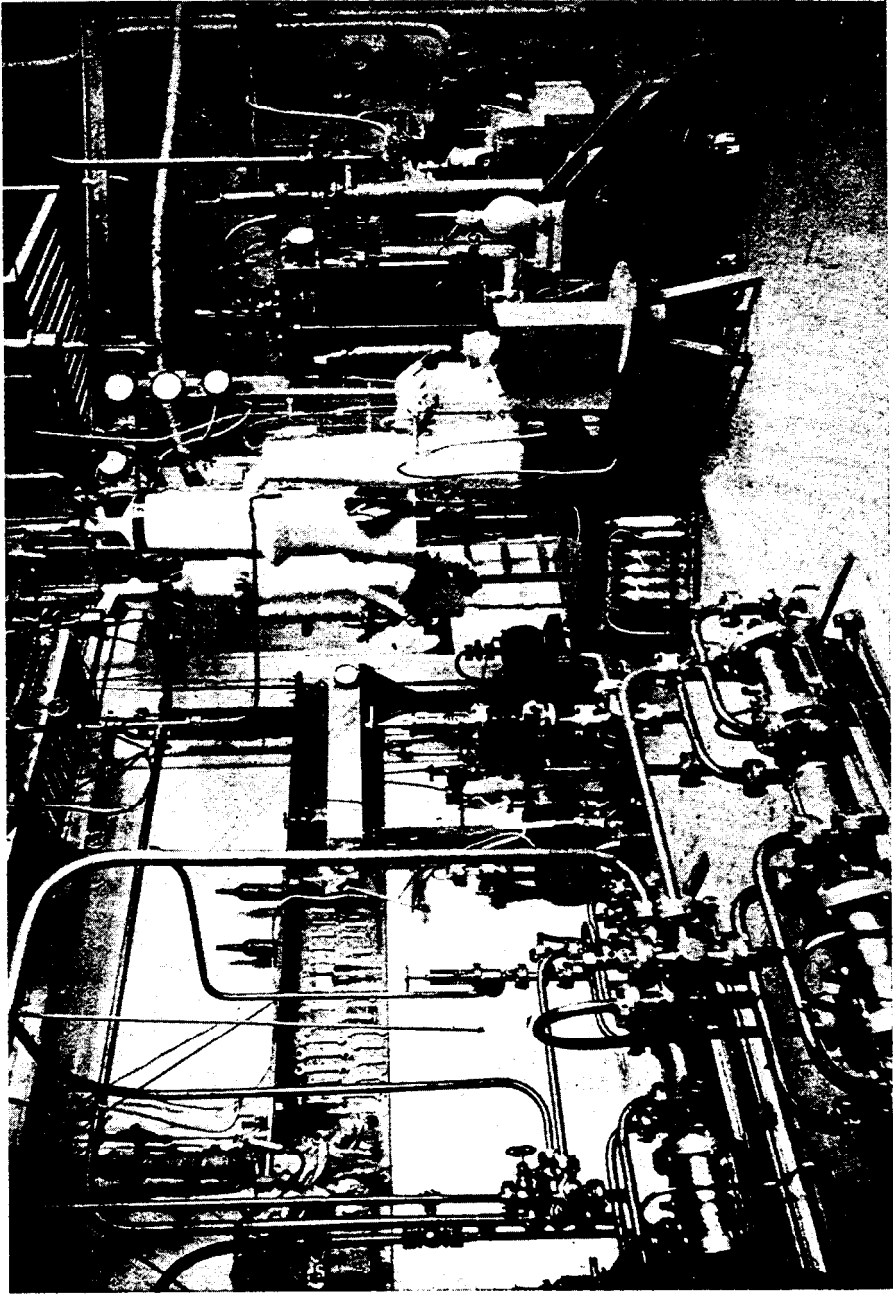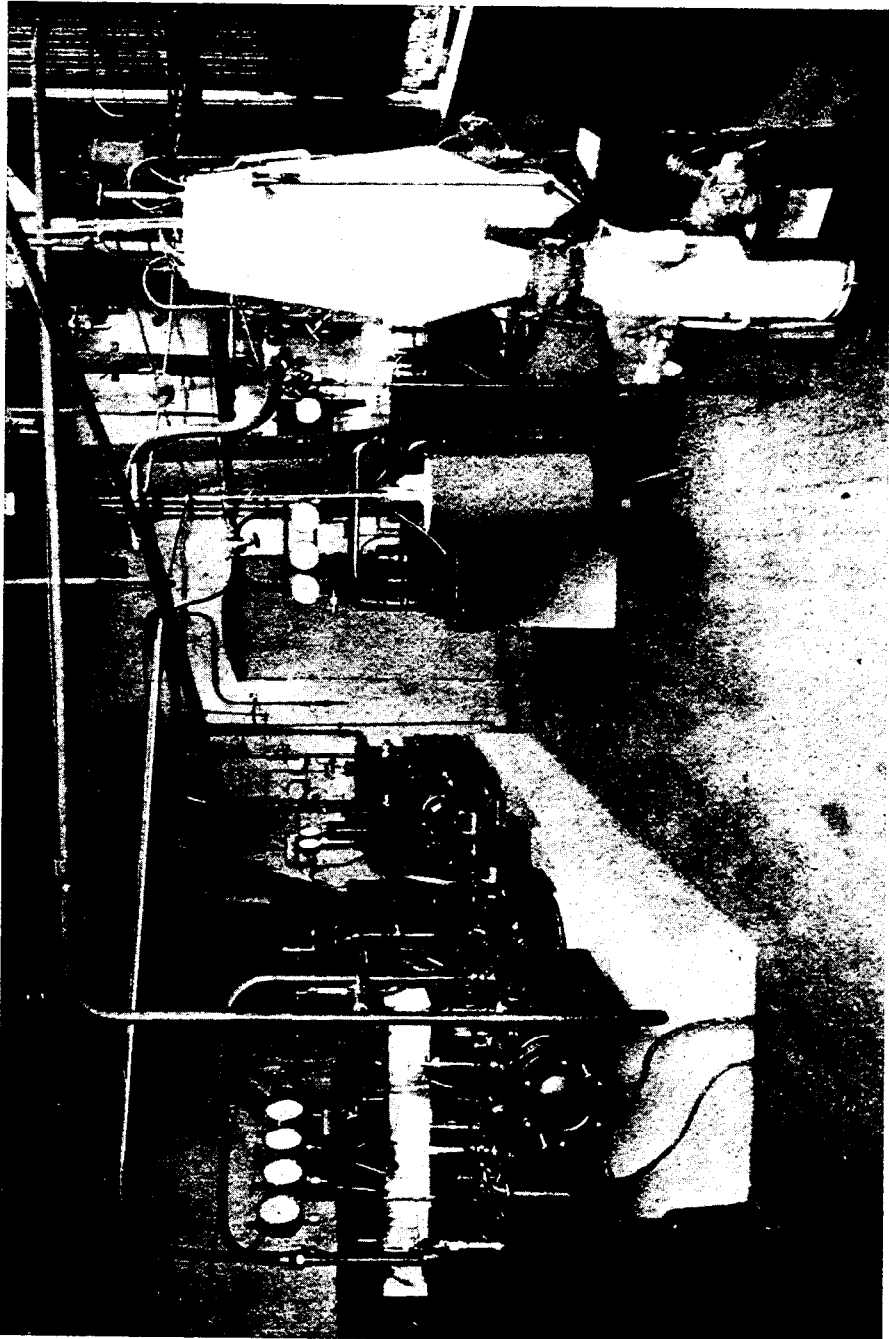
Fig. 2.

Fig. 3.

or the vacuum pumps which are so important to the working of the apparatus and which make evaporation possible under very low pressure. These are particularly important to the measurements because it is with their help that a wide temperature range can be covered with the same liquid gas.)

Let us now consider the hydrogen cycle. When I began to consider liquefying hydrogen, I started from the principle of mechanical similarity, already mentioned. From this and the critical data determined in such a masterly way by Olszewski it could be concluded that if one were successful in constructing an apparatus suitable as a model, which liquefies oxygen starting from a *normal* temperature, it would also be possible, with apparatus based on this model, to liquefy *hydrogen* starting from the temperature *of the liquid oxygen*. Long before I had the opportunity of using this principle, hydrogen had already been liquefied by Dewar. I have already discussed the great importance of Dewar's brilliant triumph for physics measurements in the rectorial address referred to above. In the liquid hydrogen we have at our disposal a freezing agent which leads us five times nearer to absolute zero than does liquid air. In Leyden a cycle which worked continuously was set up to make use of this. (Owing to the great demands made by the precision measurements which were envisaged at hydrogen temperatures, this did not come into being until many years later.) The circulation system is shown diagrammatically in Fig. 1.

The compressed hydrogen comes out of the refrigerator in which air is evaporating at the air pump, into a regenerator spiral with a throttle valve, which, following Dewar's example, is placed in a silvered vacuum glass. The spiral itself is modelled on the extremely practical Hampson apparatus for air liquefaction.

The liquid hydrogen collects in a Dewar glass and (as indicated by a float) is siphoned over into transportable, silvered vacuum glass vessels, which are connected to the container for pure hydrogen. The liquid hydrogen is siphoned out of the vacuum glass vessels in a similar way into the cryostats. It is clear that very pure hydrogen, a carefully closed cycle and special pumps must be used to circulate 40 m^3 per hour continuously, since only a little admixture of air will block up the fine ducts and valves through which the hydrogen has to flow.

The circulation is shown in the accompanying Fig. 3. The compressors, the liquefying apparatus and the vacuum pump for evaporating the liquid air in the refrigerator can easily be recognized. Much more apparatus is necessary to ensure the regular supply of 10 litres of liquid hydrogen per hour

which we now obtain and to enable the larger supplies, necessary when working with liquid helium, to be collected.

Tubing to suck the gas out of the cryostats connects the cycles described with all the working rooms. Thus, by means of liquefied gases, which evaporate under suitable pressure and which are, so to speak, as freely available as water, it is possible to maintain constant temperatures down to the freezing point of hydrogen in all parts of the laboratory.

Let us now turn to the experiments which have been carried out by this method.

Generally speaking the first task was to suit the measuring apparatuses to the method of working chosen. They had to be enclosed in an air-tight chamber, which was not always easy. It was, however, often important. For, once a cryostat of this type suitable for the experiments had been constructed, there was the advantage that one could pour the various gases one after another into the same cryostat and thus run through the whole range of low temperatures without the measuring apparatus having to be altered at all.

I cannot spend much time over this equipment (nor can I linger over that for the handling of baths, although this was often decisive for the success of difficult measurements, since it permitted the observer to concentrate all his attention on the measurements). I would prefer to put forward that the investigations in which they were used have led to a knowledge of the temperature dependence of properties of very different type. In mentioning some of these I will limit myself to those investigations which went down as far as the freezing point of hydrogen. May I first mention a few people who have collaborated with me.

Mr. J. Becquerel came to examine the absorption spectra of rare earths with and without magnetic field (Zeeman phenomenon), Messrs. Becquerel, father and son, to examine the phosphorescence of the uranyl compounds, Mr. Lenard and Mr. Pauli to examine the long-lasting phosphorescence of the alkaline earth sulphides, Mme. Curie to examine the penetrating radiation of radium, Mr. Weber to determine the viscosity of gaseous hydrogen and helium. I am particularly glad to mention that the deserving Swedish research worker Mr. Bengt Beckman and his wife came to Leyden to work on a number of problems mainly connected with his Uppsala experiments, from amongst which I name the Hall effect of alloys and the increase in resistance brought about by pressure in lead. I would like to show here (in Fig. 4) a diagram taken from a work by Dr. Beckman, in which baths of ethylene,
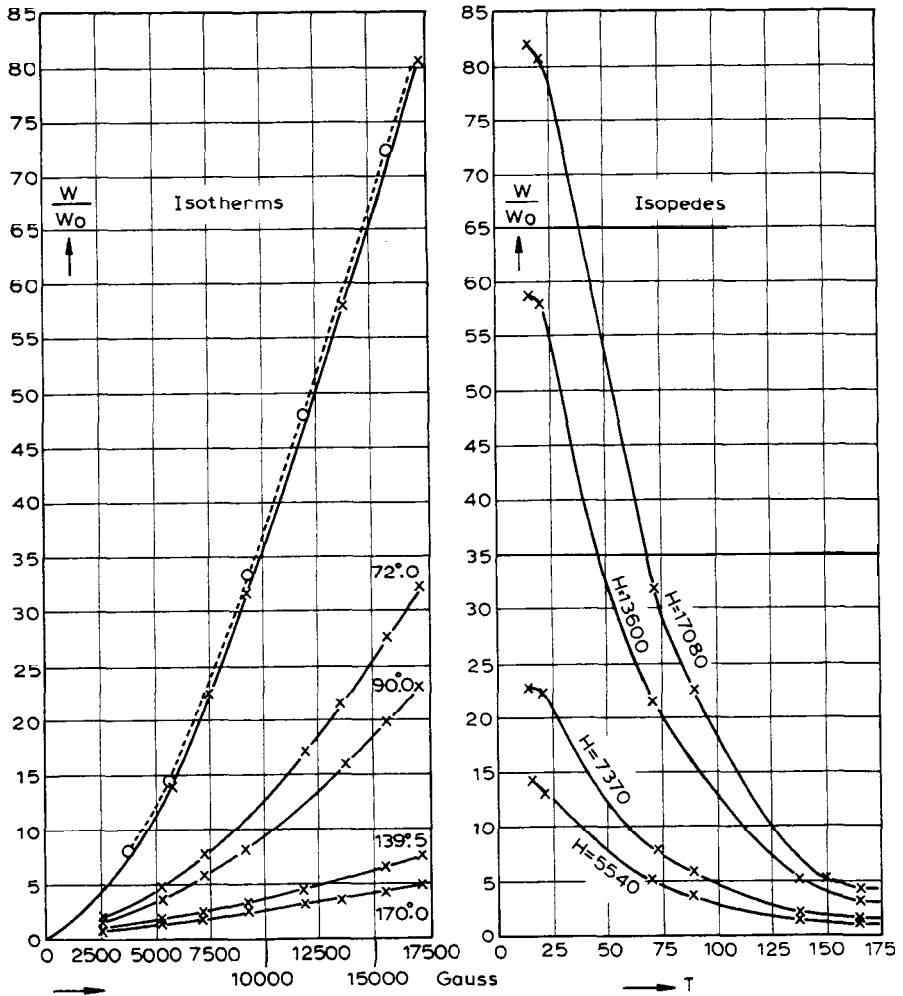
Fig. 4.

oxygen and hydrogen were used. The diagram shows to what high values the magnetic increase in resistance of bismuth rises at hydrogen temperatures.

A group particularly closely connected with the experiments last mentioned is made up of those concerned with magnetism.

Mr. Weiss came to determine the magnetic moment of the molecular magnets of ferromagnetic substances by means of saturation measurements at the melting point of hydrogen. Later, when Weiss discovered the magneton,

the results contributed to the determination of its value, which is probably fundamental to the magnetic moments of all atoms. The experiment undertaken by Mr. Perrier and myself on liquid and solid oxygen led to deviations from the Curie law, which we then found also with paramagnetic salts. During the continuation of the work with Mr. Oosterhuis it was found that one class of these deviations can be explained by assuming a Weiss molecular field with a negative sign, which then - according to investigations by Mr. Perrier and myself into the susceptibility of liquid mixtures of oxygen and nitrogen and following up Weiss' theory - could be conceived as a function of the spacing of the molecules.

The continuation of measurements on paramagnetism at helium temperatures, which has been in course of preparation for some time, is also important in connection with the theory of zero-point energy. The fact is that attempts have been made to explain deviations from the Curie law without assuming a negative field. This was on the part of Oosterhuis, in that he introduces into the Langevin theory of rotational energy, which Langevin puts as proportional to the temperature, the expression of Einstein and Stern which contains zero-point energy. If the unchanged theory of Langevin is right, however, this would be shown very clearly at helium temperatures. Also the influence of the external field on the susceptibility, which is according to the Langevin theory inversely proportional to temperature, would become clearly visible at helium temperatures in attainable fields, whilst at hydrogen temperatures it cannot be expected to the same extent until fields are reached which are ten times greater and thus far exceeding what it is possible to expect. (See Addendum 1.)

The study of the equation of state related to the monumental theories of Van der Waals has always been a main item of research in the Leyden laboratory. In particular, the exact study of the equation of state of simply constructed gases belongs to the low temperature field. Here also belong the determination of the absolute scale of temperatures below the freezing point of water. For help with the extensive precision measurements which are dealt with here I must thank my many talented co-workers. In recent times particularly Messrs. Braak, Clay, Crommelin and Dorsman, Mr. and Mrs. de Haas-Lorentz, and Messrs. Holst and Keesom have supported me and of these I have been indebted to Mr. Crommelin also for the technical running of the laboratory.

I owe much to the distinguished theoretical knowledge of Mr. Keesom and to the thorough and ingenious way in which he has worked on the the-

oretical problems connected with the equation of state, the study of which also fell mostly to his lot.

As far as the experimental work is concerned, various conditions needed to be fulfilled, each with great precision. (The law of corresponding states is roughly valid and thus only those observations are of real value the accuracy of which makes it possible to determine deviations from this law.) The pressure under which the gas is compressed, the volume which it occupies and the temperature at which the experiment takes place must be known with suitable accuracy. The volume which had to be assigned to the measuring apparatus demanded that the baths in the cryostats should sometimes have a capacity of up to 1 1/2 litres, even when working with liquid hydrogen. The temperature also had to be held evenly and constantly to within 1/100 degree in such cases.

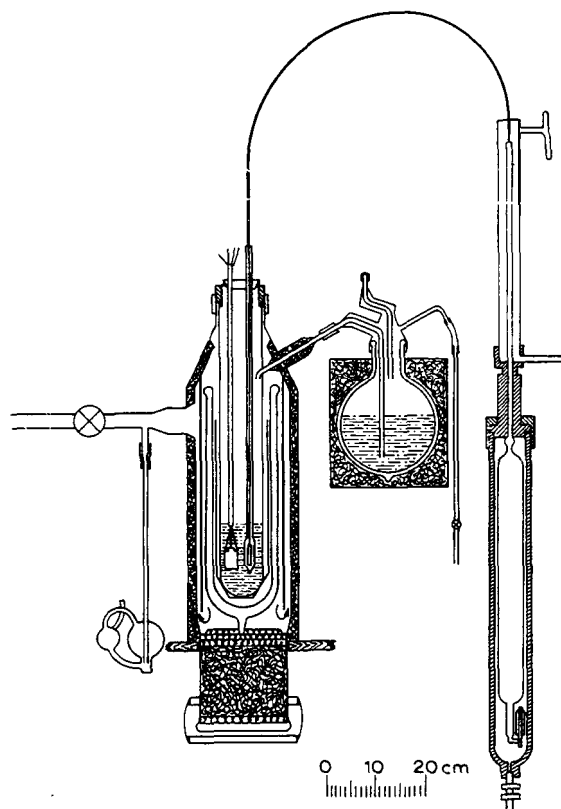(The layout of a piezometer for high pressures is shown diagramatically in

Fig. 5.

Fig. 5. The large reservoir filled with the gas to be examined is dipped into a Cailletet block and connected by a steel capillary tube to the small reservoir. The latter is in the cryostat in which the bath is maintained by one of the cycles. The gas in the piezometer is pressed by the mercury into the small reservoir. The amount of gas which is transferred is measured by the mercury rising in the calibrated column.)

In order to have a basis for pressure measurement, which would guarantee the necessary accuracy, the pressure was transferred from one to the next and so on in a series of mercury differential manometers, as shown in Fig. 6, by suitably compressed gas, so that a height of 45 metres of mercury column can be accommodated in the working room, and pressures up to 60 atmospheres measured to the nearest millimetre. (The apparatus was later extended to 90 atmospheres.)

As far as thermometry is concerned I must limit myself to mentioning that its standard was a hydrogen thermometer to which more recently a helium thermometer was also added. From the simultaneous study of all types of auxiliary thermometers down to the melting point of hydrogen it seems certain that in the absolute determination of temperatures an accuracy of 1/50 degrees is reached.

The volume gauge which was used amongst other things in the investigations into rectilinear diameter for which Mr. Mathias came to Leyden, belongs to the apparatus which serves to determine the equation of state. I must pass this by, along with much other auxiliary equipment, although I should have liked to give a better picture than is possible in this short report of the work which had to be done to determine an equation of state. Still less can I linger over the evaluation of observations. I should like, however, to mention that I obtained the virial coefficients for hydrogen with the help of Mr. Braak and Mr. de Haas, and those for argon with the help of Mr. Crommelin. Using these coefficients Mr. Keesom then did some fine work in testing various theoretical conceptions and found, amongst other things, that, as far as deviations from Boyle's law at low pressures are concerned, hydrogen behaves at low temperatures in a similar way to monatomic argon, just as was found for specific heat by Eucken.

Determination of the isotherms of helium was of the greatest importance in the liquefaction of this gas. From them information could be obtained as to whether helium, like other substances, follows the law of corresponding states, and if so what the critical data of helium are. With this information it
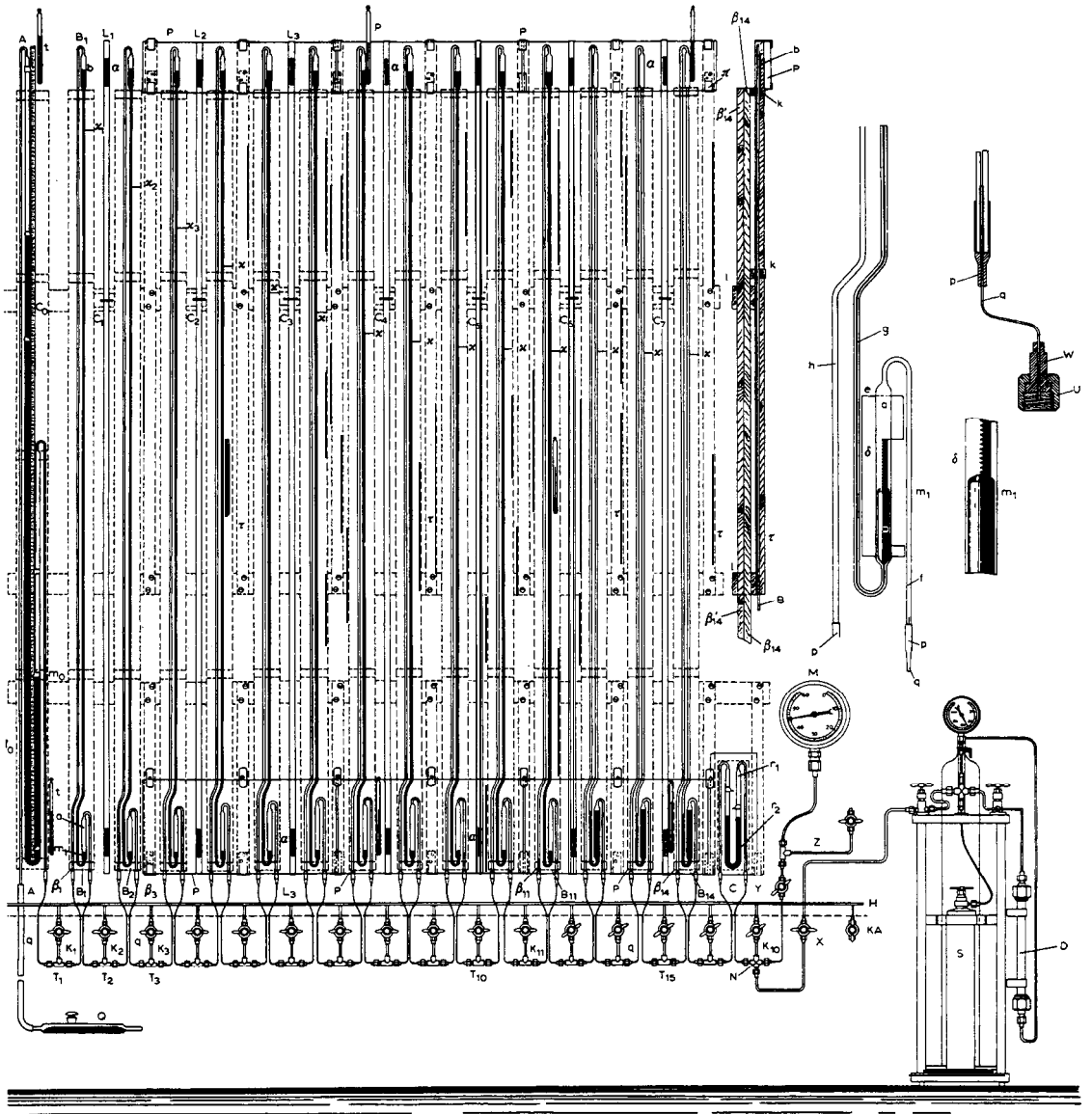
Fig. 6.

would be possible to judge whether the gas, starting from the freezing point of hydrogen, the lowest temperature to which it could be cooled, could be liquefied by means of Linde's process. If so then the principle of similarity could again be applied to the setting up of a helium cycle, just as the hydrogen liquefier had been built according to Hampson's model for an air liquefier. It became clear that it had to be found out whether the temperature at which the initial compression of the helium follows Boyle's law - the Boyle point - lies above the melting point of hydrogen. In this case one could hope for static liquefaction, if a closed helium cycle on the model of the hydrogen cycle were set up and operated in a suitable way. The question was answered in the affirmative by isotherm determination. Moreover, the compression pressure, the time the experiment would take, the cooling action to be brought about by the hydrogen cycle and also the quantity of helium necessary, were assessed as being not beyond what might be attained. As far as the helium was concerned, my brother Mr. O. Kamerlingh Onnes, the Director of the Department of Foreign Trade Relations in Amsterdam, was able to help me to obtain the necessary monazite. I am glad to be able to thank him here also.

Carrying out the experiment in the manner stated meant that the usual intermediate stage in the liquefaction of a gas would have to be by-passed by one great effort, although this bordered on the impossible. This seemed, however, the only thing to do since helium, then still such a mystery, had already so greatly disappointed me.

The accompanying Fig. 7 gives a diagram of the equipment for the experiment. The compressed helium comes, after suitable pre-cooling, into the refrigerator, where hydrogen is evaporating at the air pump, runs through the regenerator spiral and expands at the throttle valve. The liquid formed according to the Linde process gathers in the lower portion of the vacuum glass vessel. In order to be able to observe the liquid helium this portion is transparent and is surrounded by a vacuum glass vessel which is kept filled with liquid hydrogen, which is again protected by a transparent vacuum glass vessel containing liquid air, and this again by a vessel in which heated alcohol circulates.

The helium cycle, as set up, is shown again in Fig. 8 in more detail, but still in diagrammatic form, and here we find again the liquefaction apparatus; the compressors, storage flasks and regulating gas bells floating on oil are also shown. The liquefier itself is shown in more detail in Fig. 9, where the liquefying spiral built on the Hampson model can again easily be recognized.
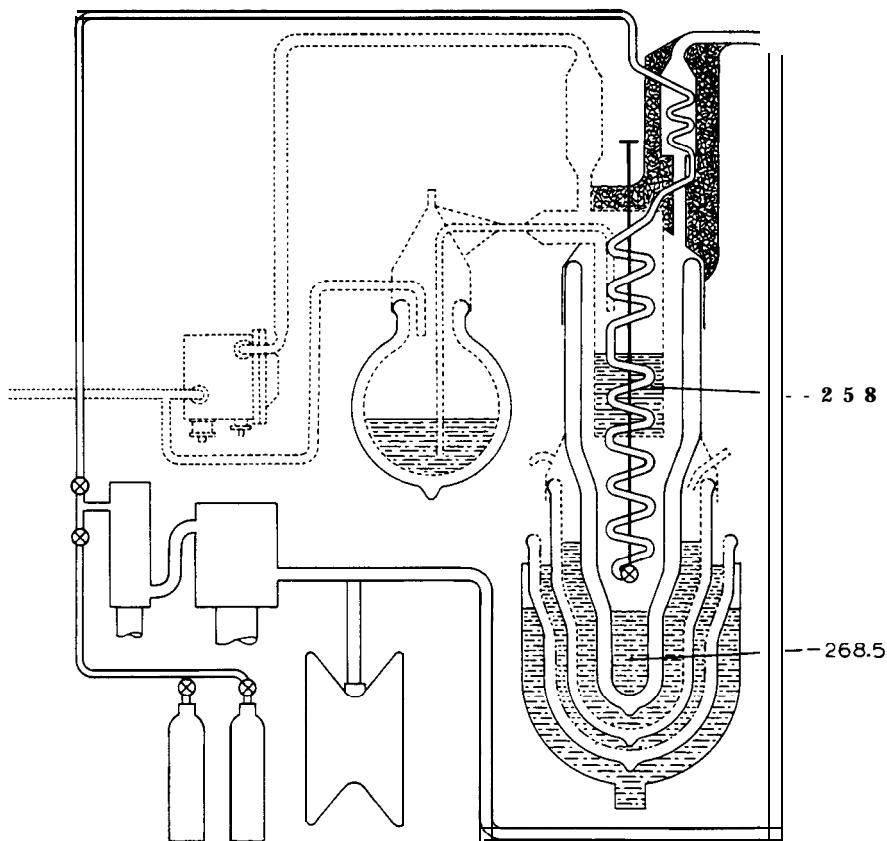
Fig. 7.

The refrigerator is supplied with liquid hydrogen from a transparent inter-
mediate reservoir, into which the liquid hydrogen is siphoned from the
storage flasks. The helium, before being cooled in the hydrogen refrigerator,
runs through a tube cooled in liquid air, with carbon to free it from traces
of air which might have contaminated it during circulation. We owe the
application of this property of carbon to Dewar. I have already stressed the
great importance of his work, but would like to emphasize here that it has
been of greatest use to me in the liquefaction of helium.

The temperature of the helium is measured with a helium gas thermom-
eter, the reservoir of which is in the liquefying chamber and is connected
by a steel capillary tube to the manometer portion.

The accompanying Fig. 10 gives a view of the whole apparatus. The trans-
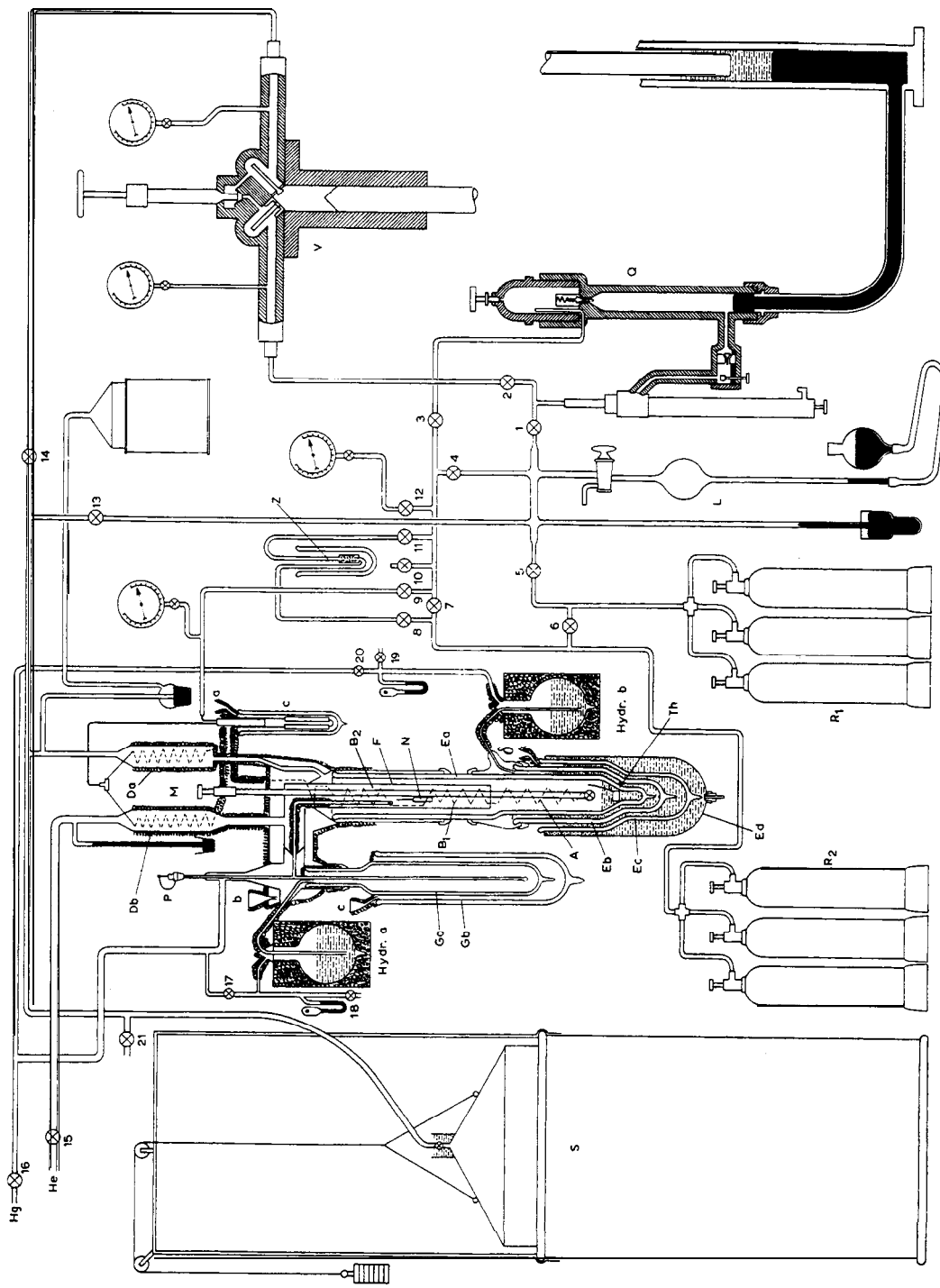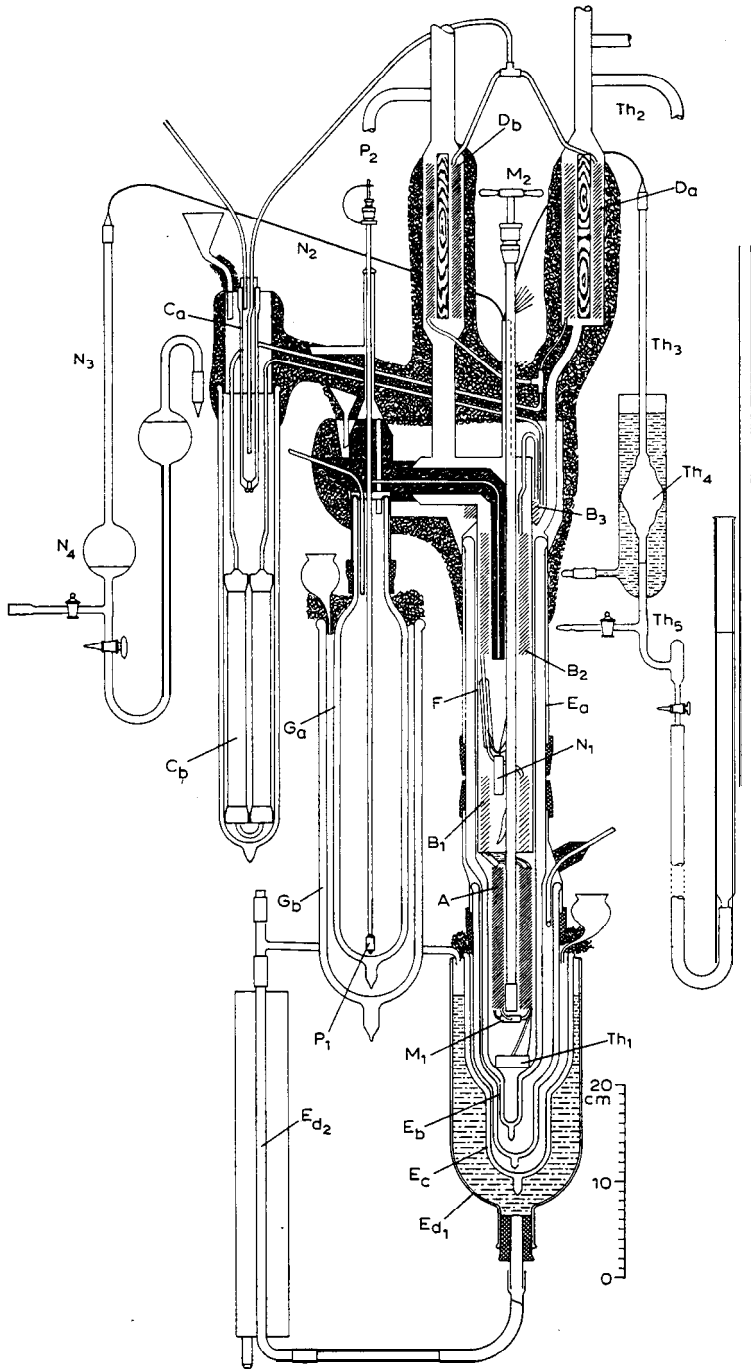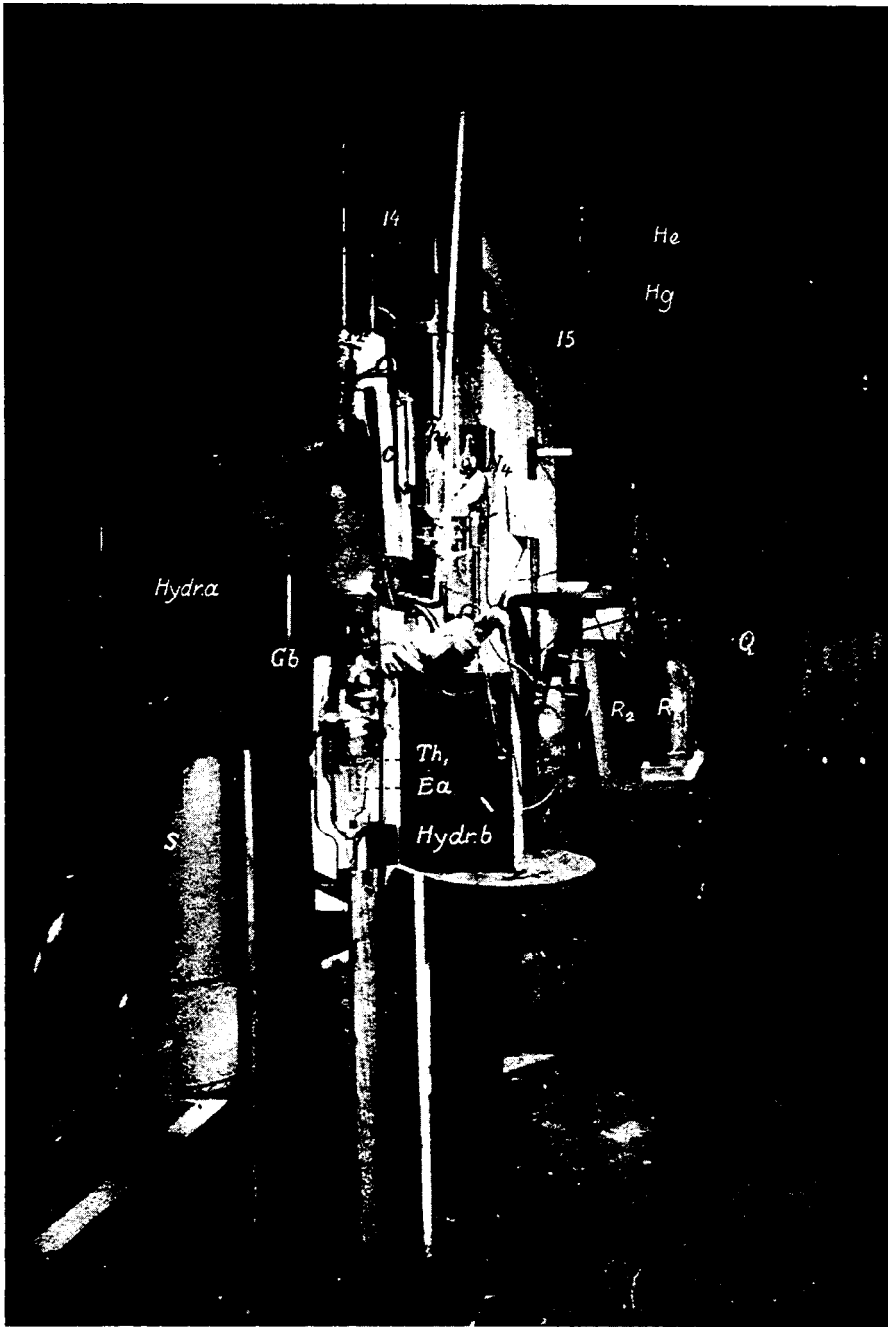
Fig. 8.

Fig. 9.

Fig. 10.

parent liquefying chamber, with three-fold protection, can be easily recognized.

As had been foreseen when the experiments were planned, their execution bordered on the impossible. By the time the experiment, which began at half past five in the morning, had ended at half past nine at night, the first helium having been seen at half past six, everyone had done everything that could possibly be demanded of him. This is particularly true of my loyal co-worker G. J. Flim, the mechanic, to whom I am also deeply grateful for help in setting up the other experiments and apparatuses discussed here.

It was a wonderful sight when the liquid, which looked almost unreal, was seen for the first time. It was not noticed when it flowed in. Its presence could not be confirmed until it had already filled up the vessel. Its surface stood sharply against the vessel like the edge of a knife.

How happy I was to be able to show condensed helium to my distinguished friend Van der Waals, whose theory had guided me to the end of my work on the liquefaction of gases.

The boiling temperature of the helium was found at 4.25°K, the critical temperature assessed as 5°K. The low critical pressure to which we had to conclude and which fell between 2 and 3 atmospheres was remarkably small.

Now that we had arrived at this elucidation of the properties of helium the next target was already indicated.

Using our knowledge, we had to make measurements and to this end, on the basis of the information obtained, to decide on arrangements which would simplify the preparation of liquid helium and make it available in a cryostat. This problem I also solved step by step. I will indicate these steps by mentioning some of the investigations already carried out with liquid helium. In these I was supported by Mr. Dorsman in the thermodynamic work and by Mr. Holst in the electrical work. I am most grateful to them.

First of all somewhat difficult conditions were encountered in the liquefying chamber. In the experiments shown in Fig. 11 considerable progress had already been made in various directions.

The experimental chamber also for these experiments is still closed off at the top by the liquefying spiral and the experiments are thus made difficult (since it is only possible to penetrate into the experimental chamber with the help of steel capillary tubes or insulated wires led past the liquefying spiral), yet a whole collection of instruments is already placed in the liquid helium. We see here a helium thermometer, the pressure of which (at 0°C 145 mm)
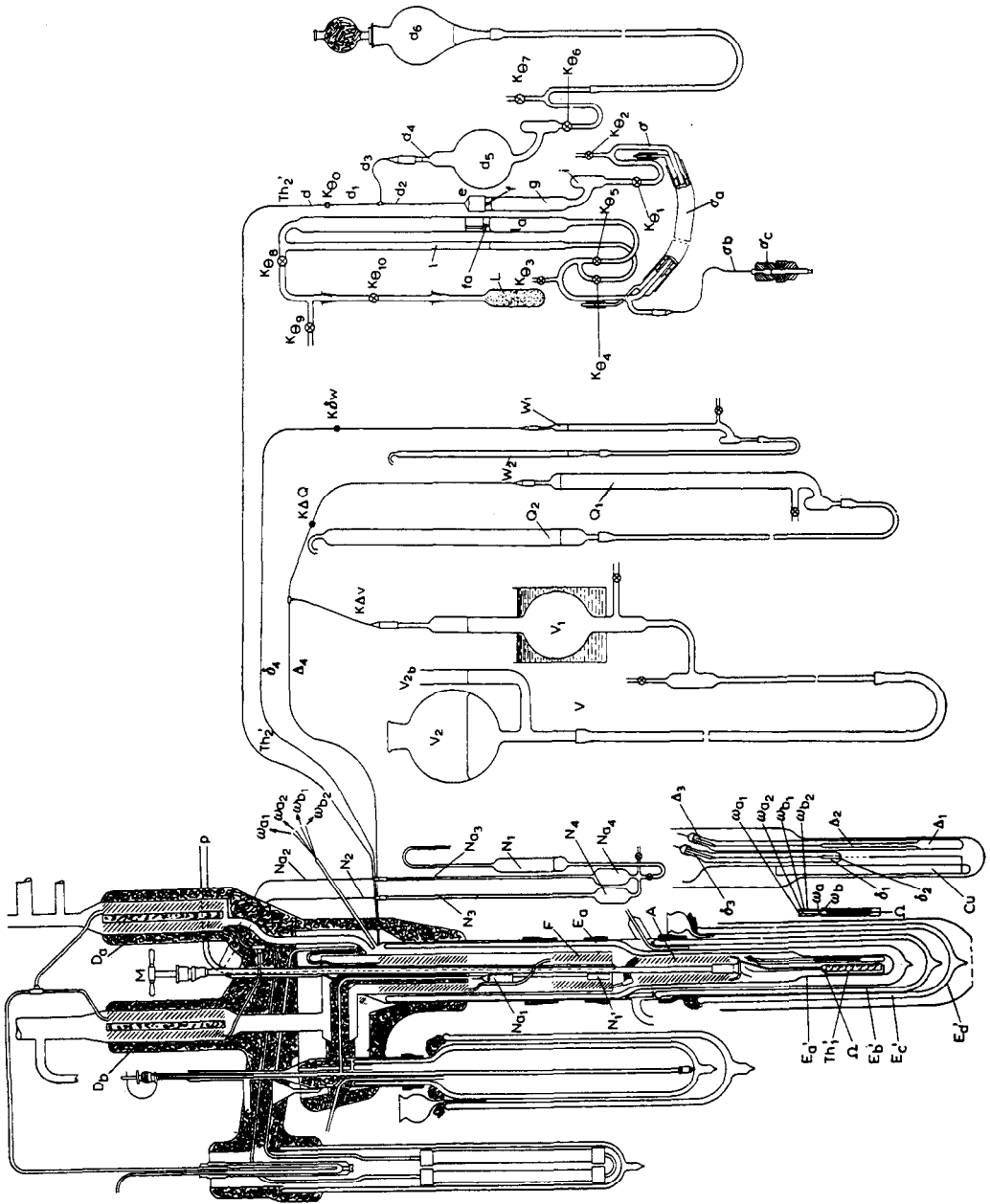
Fig. 11.

amounts to only 3 mm at the boiling point of helium, so that temperatures down to 1.5°K approximately could be measured with it. Here the accuracy of the measurement was suited to the smallness of the pressure.

The simultaneous measurement of the pressure in the chamber in which the liquid helium evaporates yielded the law of vapour pressure. To measure how the density of the liquid helium changes with the temperature there was also in the helium bath a differential dilatometer (into which volumetrically measured quantities of helium were brought through two identical steel capillary tubes).

It is very noticeable that the experiments indicate that the density of the helium, which at first quickly drops with the temperature, reaches a maximum at 2.2°K approximately, and if one goes down further even drops again. Such an extreme could possibly be connected with the quantum theory. At any rate, closer examination of the equation of state of the helium in relation to deviations from the law of corresponding states is very promising, as it is the critical temperature precisely of this gas which approaches absolute zero so closely.

Naturally the question arose as to whether helium can also be converted into the solid state. An experiment aimed at lowering the temperature of helium sufficiently by evaporating it without supply of heat was not successful, and only served to reach the lowest temperature recorded up to that time. The helium (see Fig. 12) evaporating in a vacuum glass vessel was protected against heat supply, the vessel itself being dipped in a bath of liquid helium. The bath was obtained, as the figure shows, by the liquid helium flowing out of the liquefying apparatus into a cryostatic vessel.

The evaporation of even a very small quantity, when the pressure of the vapour is small, demands the continuous carrying away of colossal volumes of vapour. With vacuum pumps of very large capacity we succeeded in lowering the pressure to 0.2 millimetre. The temperature then reached was 1.15°K according to the law of vapour pressure found. (Of course we can only make an estimate here. The working out of the thermometry of these low temperatures with, amongst other things, the aid of the Knudsen hot wire manometer is still in its initial stages.) Since it would have needed new equipment, I deferred the question as to whether helium can be made to freeze in favour of other, more urgent problems, which could be tackled with the equipment available.

The handling of these questions was very considerably facilitated when we succeeded in getting the cryostat shown in Fig. 13 to work. The liquid he-
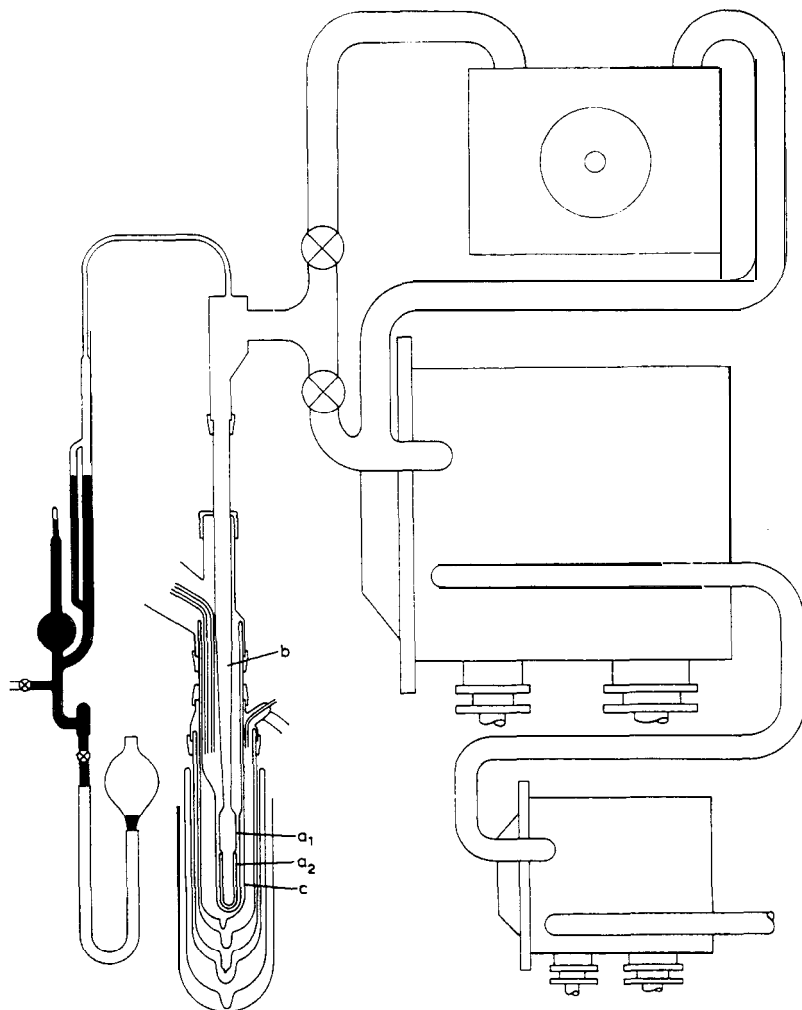
Fig. 12.

lium is siphoned over from the liquefier into a cryostatic vessel open at the top (through a vacuum tube cooled with liquid air). The liquefier can be shut off from the cryostat by a valve. In this way continuous working of the liquefier was possible. The bath is stirred vigorously by an electromagnetically-driven pump.

With this cryostat, investigations into the extraordinarily great conductivity of some metals at low temperatures were possible, and I wish now to report on these;

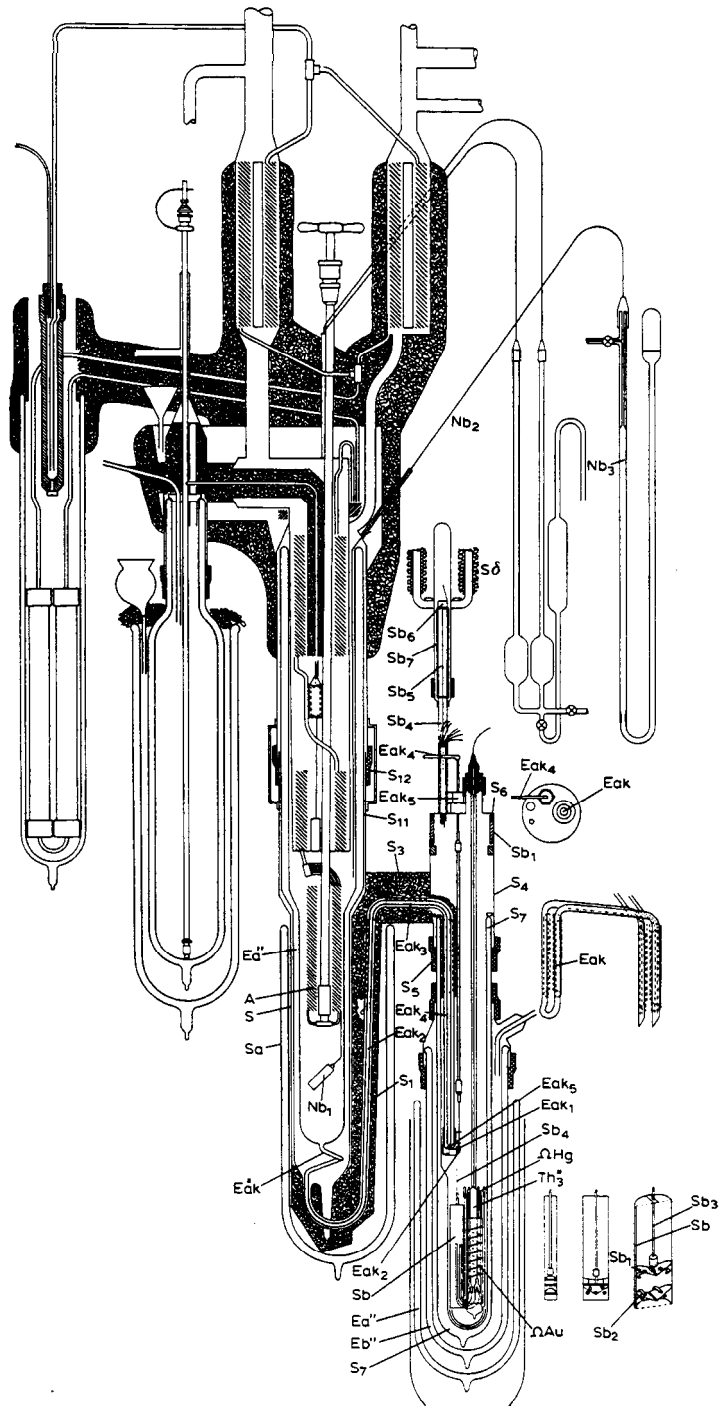Even the very first experiments on the resistance of metals had brought

Fig. 13.

very surprising results. With platinum wire there was no re-rise in resistance after reaching a minimum, as would be expected, if the electrons which provide the conduction were firmly frozen to the atoms at low temperatures, but on the contrary resistance became independent of temperature. The conclusion drawn from the results of an experiment carried out with Mr. Clay down to the freezing point of hydrogen was that for absolutely pure platinum resistance would disappear at the boiling point of helium. At the lowest temperature therefore the conduction electrons are not bound but the factors which hinder their movement disappear. The obvious thing was to look for these hindering factors in the energy of Planck's vibrators, so that here the theory of resistance agrees very well with that of specific heat.

I attributed the fact that the resistance had become constant and not zero to the slight impurities which remain even in pure gold. I could only hope to get the mercury purer than gold, and the observations just made permit one to conclude that its resistance at the boiling point of helium would still be observable but that at the lowest temperature that could be reached with helium it would disappear. The possibility of confirming this caused me to think of little account all the difficulties which were attached to the experiment. These were overcome and the results are, as Fig. 14 shows, convincing. The resistance, in fractions of the resistance at zero Centigrade, is shown as the ordinate and the temperature as the abscissa. The figure contains, as well as the results obtained in helium, which are marked II, also those, marked I,
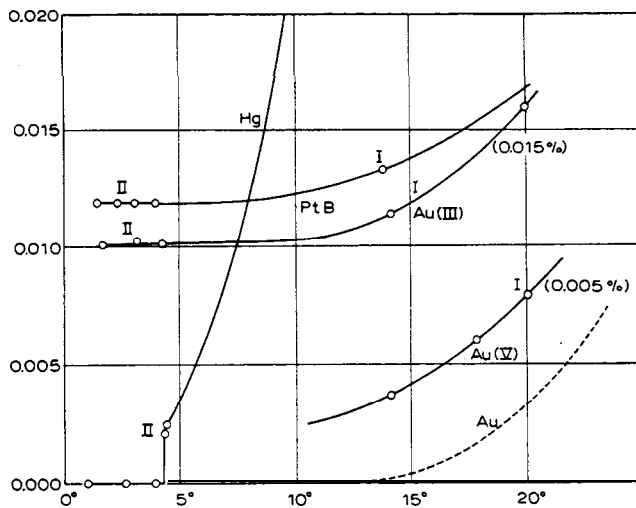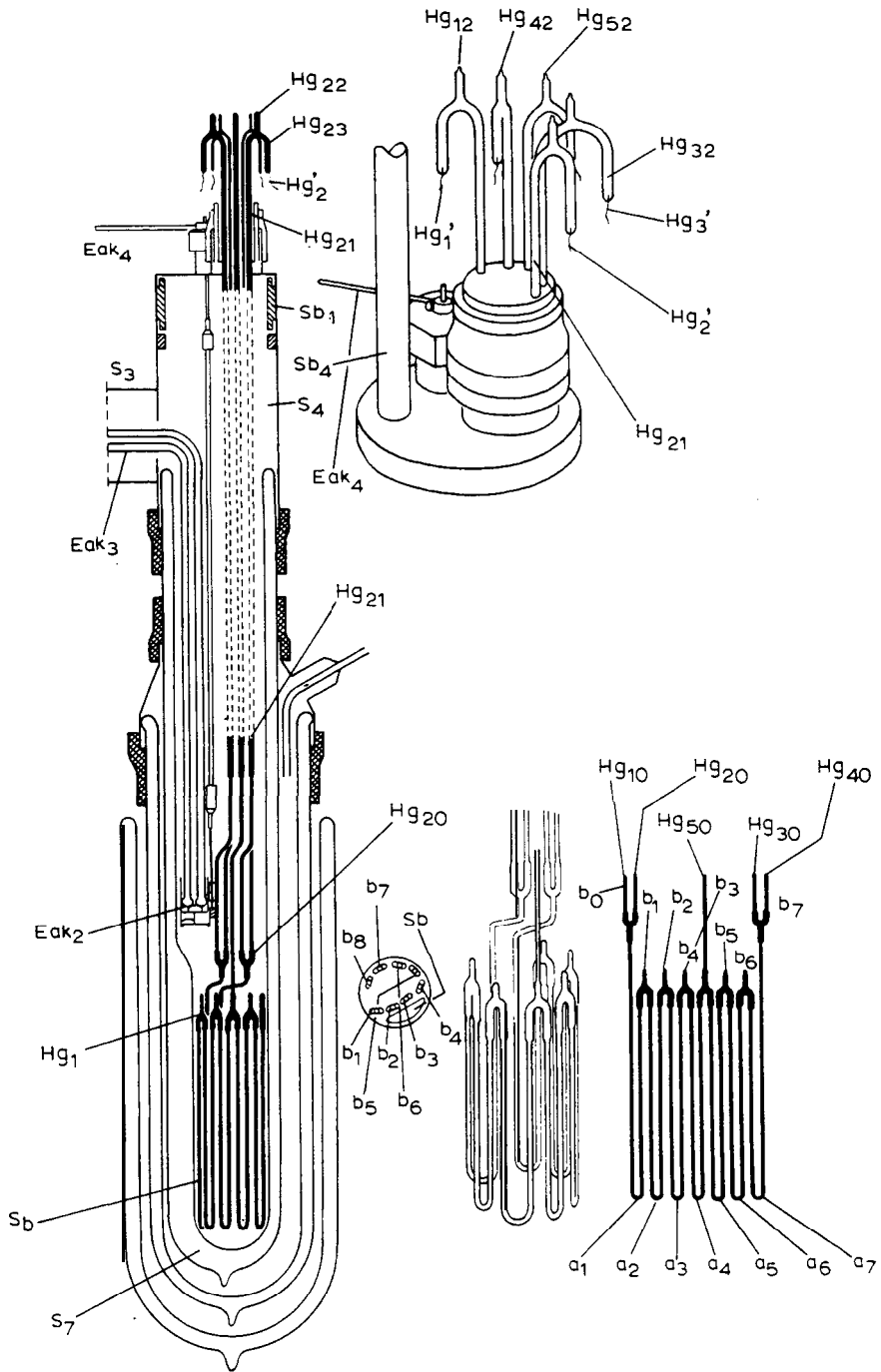

Fig. 14

Fig. 15.

which had been found in the course of investigations carried out by Mr. Clay down to the melting point of hydrogen. The resistance of the mercury is indicated by *Hg.* The results for platinum and for gold are also given in the figure, as well as the hypothetical curve for pure gold, the latter shown as a dashed line.

I would like to spend a little time on the arrangement of the experiment.

The thread of mercury, the resistance of which was measured, is shown in the accompanying Fig. 15. The mercury, which had been painstakingly pur-ified, is poured off into a series of U-shaped capillary tubes of only 1/20 millimetre diameter in vacuo and frozen in them during the experiment. At the upper ends of the U there are (see Fig. 16) reservoirs to deal with the change in the volume of the mercury. It is, however, difficult to avoid the
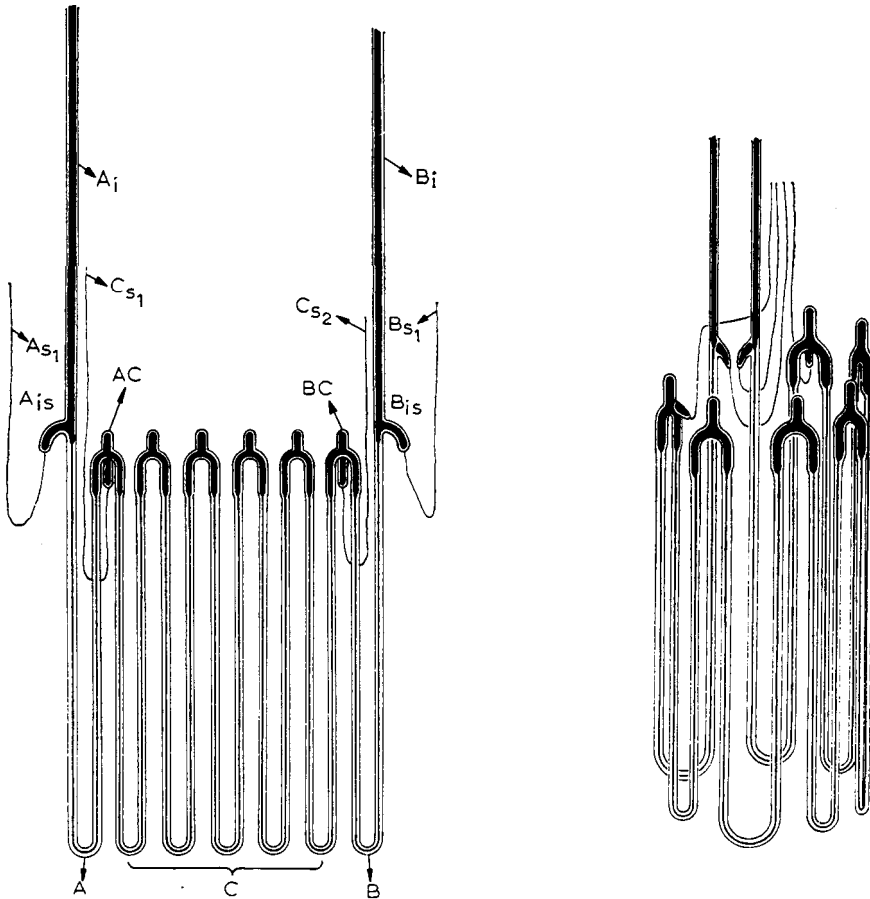

Fig. 16.

tubes bursting or the thread breaking either during thawing or freezing. At the ends of the resistances there are mercury wires to conduct the current and to measure potential differences. (This is the most simple model theoretically: a branched wire system all of the same metal. In the following model, see Fig. 16, the lower portions of the voltage wires are replaced by platinum wires.)

As has been said, the experiment left no doubt that, as far as accuracy of measurement went, the resistance disappeared. At the same time, however, something unexpected occurred. The disappearance did not take place gradually but (compare Fig. 17) *abruptly*. From 1/500 the resistance at 4.2°K drops to a millionth part. At the lowest temperature, 1.5°K, it could be established that the resistance had become less than a thousand-millionth part of that at normal temperature.

Thus the mercury at 4.2°K has entered a new state, which, owing to its particular electrical properties, can be called the state of superconductivity.

It is very important to the study of the properties of this state that tin and lead can also become superconductive. The transition point of tin lies at 3.8°K, that of lead probably at 6°K. Now that we are able to use these metals, which are easy to work, all types of electrical experiments with resistance-free apparatus have become possible. To take one example: a self-contained coil, cooled in the magnetic field, should, when the field is removed,
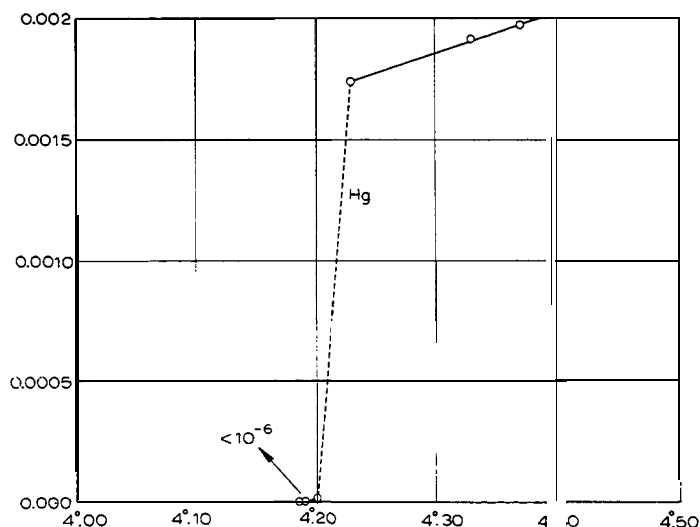

Fig. 17.

be able to simulate for some time an Ampère molecular current. (See Addendum 2.) There is also the question as to whether the absence of Joule heat makes feasible the production of strong magnetic fields using coils without iron,* for a current of very great density can be sent through very fine, closely wound wire spirals. Thus we were successful in sending a current of 0.8 amperes, i.e. of 56 amperes per square millimetre, through a coil, which contained 1,000 turns of a diameter of 1/70 square mm per square centimetre at right angles to the turns.

All that I have said so far about superconductors applies only to currents below a certain threshold value, which lies all the higher the lower one drops in temperature. Up to this threshold value of current intensities no potential differences are found at the ends of the resistance within the degree of accuracy reached so far. The wire has at the most only a residual micro-resistance. As soon, however, as the threshold value is exceeded, a potential difference is necessary to maintain the current. Then, in a way as yet unexplained, normal resistance occurs in the wire, and at the great rate at which the potential difference is increased at the ends, there can be a considerable rise in temperature. Thus a bright lead wire which had been dipped in liquid helium and which remained superconductive up to a current density of 4.20 amps. per square millimetre, melted at a current density of 940. It appears

* Shortly before this lecture I still felt that further experiments would lead to this question being answered in the affirmative. For if the contrary were the case new phenomena would have to be found. It seems possible that the potential phenomena which will be further discussed in the text can be suppressed by improving the material and the construction of the coil. Then only the resistance would be need to be considered which, owing to the characteristic magnetic field of the coil, can be produced in the resistanceless wire. After the experiment with the small coil mentioned in the text, it seemed that even this resistance would not come into the picture very much, even when strong fields are produced. From analogy it was to be assumed that it rises regularly with the field and even when it is proportional to the square of the field it would not be of very great importance even in fields of 100,000 Gauss, as the resistance produced in the coil by its own field was anyway still unnoticeable. Only experiments, however, could make certain of this. The experiments then planned were carried out after this lecture was given and produced surprising results. In fields below a threshold value (for lead at the boiling point of helium 600 Gauss), which was not reached during the experiment with the small coil mentioned in the text, there is no magnetic resistance at all. In fields above this threshold value a relatively large resistance arises at once, and grows considerably with the field. Thus in an unexpected way a difficulty in the production of intensive magnetic fields with coils without iron faced us. The discovery of the strange property which causes this made up for the difficulties involved.

that, generally speaking, when the threshold value of the current intensity is exceeded, local heating of the conductor through which the current is passing occurs above the transition temperature and this is why normal resistance at this point originates. When the current intensity increases the Joule heat produced at this point soon brings the whole resistance above the transition point.

The great question still not solved is whether this first impulse proceeds from bad sections of the wire or is also produced in pure, tension-free, evenly crystallized metal. If the potential phenomena are to be attributed to bad spots, we shall learn to eliminate them and then it is perhaps possible that the conductivity could be increased still higher than to the value reached at present, which is thousand million times that at normal temperature. The potential phenomena may, however, depend upon the nature of the metal in that the resting vibrators of the now superconductive metal are not made to move until the electron wind which blows past them has reached a certain strength, just as the surface of water is not ruffled until the wind has reached a certain strength. Ohm's law would have lost its validity for these phenomena.

Rather than immersing myself in a possible explanation based on the quantum theory, I should like to consider one of the experimental questions raised by the superconductors. According to ordinary theory of electrons one finds, for the free paths of the electrons, which at normal temperature are about of molecular size, values for the superconductive state going up to a metre. Will superconductive foils be passed through more easily, or with less deflection, by electric rays of various types than are ordinary conductive ones? This question has been raised by Mr. Lenard and myself. Mr. Becker and I are already busy with the relevant preliminary experiments.

I have already said that this is only one of the many questions which the superconductors raise. From each field of physics further questions push their way to the fore which are waiting to be solved by measurements at helium temperatures.

In the future I see all over the Leyden laboratory measurements being made in cryostats, to which liquid helium is transported just as the other liquid gases now are, and in which this gas also, one might say, will be as freely available as water.

In the meantime there is plenty of work which can already be done, albeit with difficulty (as when we began to use liquid oxygen), in the neighbourhood of the liquefying apparatus, and which can contribute towards lifting the veil which thermal motion at normal temperature spreads over the inner world of atoms and electrons.

Added in proof

1. In May 1914 the qualitative validity of the Langevin theory in both the connections mentioned in the text was established in gadolinium sulphate by experiments at helium temperatures.

2. The following was achieved during the experiments carried out in April-June 1914 relating to currents persisting in superconductors in the absence of electromotive force. The current, once produced, lasted for hours practically unchanged in the superconductive coil. Heating the latter above the transition point immediately destroys the electromagnetic field borne by the circuit. The experiments evidently demonstrate the frictionless mechanism as envisaged by Maxwell in the ether around a circuit and the absorption of its kinetic energy by a resistance introduced into the circuit.