One of Onnes' first papers on the low temperature resistance of elemental metals after successfully establishing in his laboratory a reliable facility to measure the physical properties of materials at the boiling point of He. This paper discusses initial measurements on platinum...ironically used as the thermometer in many subsequent measurements at Leiden.

COMMUNICATIONS

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UNIVERSITY OF LEIDEN

BY

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No. 119.

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H. KAMERLINGH ONNES. "Further experiments with liquid helium. A. Isotherms of monatomic gases etc. VIII. Thermal properties of helium.

B. On the change in the resistance of pure metals at very low temperatures etc. III. The resistance of platinum at helium temperatures". (*With three plates*).

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H. KAMERLINGH ONNES. "*Further experiments with liquid helium.*"

(Communicated to the Meeting of Dec. 24, 1910).

A. *Isotherms of monatomic gases etc.* VIII. *Thermal properties of helium.*

§ 1. *The Helium-bath.* In most of the experiments that one would like to make at helium temperatures, it is necessary to transfer the liquid helium from the apparatus in which it has been prepared to another — the helium cryostat — more suitable for holding the apparatus arranged for these special experiments. In Comm. N°. 112 (June 1909) it was mentioned that this was going to be tried; and in the Jubilee book presented to J. M. VAN BEMMELEN it was further stated that the transference had, in fact, been once successfully accomplished. Although the success which attended this operation allowed immersion in the protected helium bath of the apparatus with which it was shown that even at a vapour pressure as low as 0.15 mm. helium is still a liquid, it was nevertheless evident that this desirable result had been obtained only by accident. A method that promises to be more efficient is now being developed, and I hope to be able to make a communication in the near future concerning it.

In the meantime, a few problems could already be studied with the help of a liquefying apparatus resembling the original liquefying apparatus (Comm. N°. 108, Aug. 1908) sufficiently well to ensure that when an experimental apparatus is introduced into its interior this experimental apparatus would also be surrounded with liquid helium. To be certain that this was the case, it was necessary that the principle of the original liquefying apparatus should not be altered in any way, and, hence, the difficulty that the liquid helium would be contained in a space that is practically closed above by the regenerator spiral could not be avoided. But this space destined to contain the liquid helium could still be made as large as was found permissible from the experience gained with the liquefying apparatus. An apparatus was, therefore, constructed to hold a thermometer reservoir of greater dimensions than the one which had been used up till 1909, a resistance thermometer such as was used in the investigation of the electrical resistance at hydrogen temperatures, a dilatometer of dimensions greater than those given in Comm. N°. 112, and also a control dilatometer.

The apparatus is shown in Fig. 1 Pl. I [1]). The letters are the same as in Pl. III of Comm. N°. 108, and are accented where one of the parts has been modified. Moreover, Pl. II of that Communication holds for the helium cycle as far as its use at ordinary pressure is concerned. To allow the helium to evaporate under lower pressure the tube that leads the gas off from the liquefier is coupled to the wide exhaust of a BURCKHARDT vacuum pump capable of transplacing 360 m³ per hour. To follow this operation the part D_a and those attached to it in Pl. II Comm. N°. 108 must be replaced by the modifications shown in Pl. II fig. 1; connectión with the pump is made through *Bu Va* and this is closed by the tap 22; while 23 in a bypass allows a fine adjustment of the quantity of the gas that is being removed; 24 and 25 allow the gasometer and the liquefier to be independently evacuated (see Pl. II Comm. N°. 108).

Besides the changes in the apparatus necessary to enable it to contain the measuring apparatus, it remains to be remarked that a second helium thermometer Na_1, Na_2, Na_3, now serves to indicate the quantity of liquid hydrogen present in F instead of the two thermocouples that were formerly used in conjunction with the small helium thermometer (now N_1', N_2, N_3). The position of the liquid surface in F can be ascertained much more easily from the motion of the mercury in the capillaries N_3 and Na_3 than was possible with the more round-about thermocouple measurements; the liquid hydrogen can therefore be used more sparingly, and the tedious preparatory work of adjustment necessary for these experiments can be shortened.

In the lower part — the cryostat space — of the glass E'_a (fig. 1 and fig. 2) is the reservoir Th' of the helium thermometer, with which the temperature of the bath is determined, the resistance Ω, the dilatometer Δ, and the control apparatus of the dilatometer δ. And finally, a thick copper rod *Cu* is also placed in it so that, since the liquid in the bath cannot be stirred, conduction along the rod may keep the temperature of the bath more equable at all points. The narrow space between the regenerator spiral A and the wall of the vacuum glass E_a' is filled with flannel, and now three capillaries pass through it instead of the single thermometer capillary (that of Th_1 Pl. III Comm. N°. 108). One of these, Th'_2, leads to the thermometer (replacing Th_1, Th_2, Th_3, Th_4, of Pl. III, Comm. N°. 108), the second to the dilatometer (this was already used in Comm. N°. 112), and the third to the control apparatus of the dilatometer (connecting δ with W). Furthermore, instead of the two insulated wires of the thermocouple (Comm. N° 108) four insulated wires W_{a_1}, W_{a_2}, W_{b_1}, W_{b_2}, now pass through this space; these are the pairs of wires that lead the current to and from the resistance Ω.

All these capillaries and insulated wires must pass through the space that is filled with liquid air, which must still remain airtight (this space is described under *d* of Comm. N°. 108 § 2, and *b* Pl. II of that Comm. shows how liquid air is introduced). This is accomplished by soldering the capillaries to the new-silver wall of the liquid air vessel, while the insulated leads are enclosed in new-silver tubes that pass through the wall and are soldered to it.

The operation of filling the lower portion E_{a_1} (Pl. I fig. 1) with liquid helium is conducted in exactly the same way as is described in § 4 Comm. N°. 108. Practice in the various operations and the improvement made by introducing the second helium thermometer rendered it possible to save a fair amount of liquid hydrogen so that, as a part of the necessary hydrogen had been liquefied the previous day, it was possible to begin at half past seven in the morning and to have the cryostat part of the apparatus full of liquid helium by a quarter to two in the afternoon. The circulation pressure was kept at 25 atmospheres (cf. § 2, Comm. N°. 112).

The pressure under which the helium vaporizes is derived from the pressure obtaining in the wide space beneath the german silver chamber F; from this space a tube passes through F and comes outside the apparatus at p_1; it is there coupled to the

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[1]) The alcohol glass with its attachments (cf. Pl. III, Comm. N°. 108) *Ed* is only partially shown in the drawing.

apparatus for regulating and measuring the pressure. The difference of pressure between this space and the surface of the liquid helium necessary to drive the vapour up between the coils of the regenerator spiral was found, from measurements made with air, to be less than 1/20 mm., and may, therefore, be left out of account. Only at very low pressures will a correction be necessary for it in obtaining very accurate results.

Fig. 2, Pl. II shows the apparatus that serves to regulate the quantity of gas pumped off through the exit valves; by such regulation the temperature of the cryostat part of the apparatus is kept as constant as possible, and from its constancy one can judge how far the vapour pressure remains invariable; it also shows how this pressure is measured. For pressures greater than 5 cm. the gauge I_1 is used, for pressures between 5 cm. and 1 cm. I_2, and for pressures lower than 1 cm. I_3. By opening K_{i21}, K_{i22}, K_{i23}, or K_{i31}, K_{i32}, K_{i33}, I_{2a} or I_{3a}, as the case may be, is brought to a definite pressure which is measured by I_1 or by the MACLEOD gauge I_4; K_{i21} or K_{i31} is then closed, and the taps regulating the rate at which the gas is pumped off are operated so that the oil in the graduated sloping tubes of the indicators remains at the same mark.

Any definite pressure and, therefore, any definite temperature at the surface of the liquid in the cryostat can be quite satisfactorily obtained. The temperature of the bath, however, is less assured, since stirring is not possible, and the conductivity of *Cu* offers but slight compensation for this defect. The lower parts of the bath are at a higher temperature, and the corresponding vapour pressure may be increased by 0.009 to 0.011 mm. of mercury per mm. distance from the surface of the liquid helium; at the lowest temperatures this is equivalent to a temperature difference of 0.06 degree, and with this uncertainty we must be content as long as we have not at our disposal a cryostat in which stirring is possible; it is not, however, greater than uncertainties arising from other causes that are already present.

§ 2. *The Thermometer.* Temperatures were measured by means of a constant volume helium thermometer of zero pressure = 14.5 cm. (Cf. Comm. N°. 112).

At the lowest measured temperature, the pressure of the gas in the thermometer was 1.2 mm., and the vapour pressure of the helium was only 2 mm. The circumstances of measurement were, therefore, pretty much the same with respect to helium as if a constant volume ether vapour thermometer were used for determining ordinary atmospheric temperatures. In the present case there is, moreover, the particularly small value of the pressure itself to be taken into account. Hence, in the very nature of the determinations themselves there is cause for many uncertainties. In the meantime, however, it seems best to make a beginning by assuming that the ordinary gas laws may still be applied at the very small densities, and to postpone the application of corrections for the deviations that should differ from those according to the law of corresponding states and for possible condensation of vapour on the walls, etc., until experiments have been completed which will afford an estimate of these corrections. In this way one can at least attempt to obtain data concerning certain thermal properties of helium. I mentioned in Comm. N°. 112 that at that time I had not been successful in overcoming the difficulties that are always encountered when making measurements with a thermometer, built on the principle of the one that has hitherto been used, in the immediate neighbourhood of apparatus that are used for the preparation of liquid helium. These difficulties have not yet been wholly removed. The necessity for simplicity and ease of manipulation of the apparatus, and the fact that the thermometric measurements should be independent of all vibration and all disturbances arising from other operations are difficult to reconcile. But still, it would appear that the temperatures obtained may be relied upon to within 1/10th of a degree.

The part of the helium thermometer that serves for the adjustment of the constant volume, and for the reading of the pressure is shown on the right hand side of Plate I. Its arrangement is similar to that of the hydrogen thermometer shown on Plate I of Comm. N°. 95*e* (Sept. 1906) when this is being used for measuring hydrogen temperatures; part of the lettering is chosen so as to correspond with that of the latter plate. On account of the smallness of the pressures to be measured at the helium temperatures the space above the mercury in the adjustable double manometer tube l and f_a is evacuated, and, to make quite certain, they are connected to an evacuated tube L filled with charcoal and immersed in liquid air. The manometer tube on which the pressures are read off, has, as well as the adjusting tube, a small steel point, so that the difference of level between the two mercury menisci may be obtained with greater accuracy. The base e_a which carries the point f_a is slotted, as can be seen in the figure. Before making any adjustments the tap $K\vartheta_5$ is closed, and it is opened to allow communication between the mercury in the reading tube and that in the adjusting tube of the manometer only after the mercury meniscus in the adjusting tube has been brought to the level of the point f_a in the reading tube by opening $K\vartheta_1$ and moving the double manometer tube up and down until this is accomplished. Then to proceed to an adjustment the adjusting tube can be shut off with $K\vartheta_4$. By a slight turn of the screw s_c and of the screw with which the fine adjustment of the height of the manometer tube is obtained, both of which are within the observer's reach, the mercury surfaces are brought as near as possible to the two points; the height of the mid point between each point and its mirror image is then ascertained with the cathetometer provided with one of the reading microscopes of Comm. N°. 85 (June 1903) and of Comm. N°. 95*b* (June 1906) when the cathetometer was used as a vertical comparator.

In this way, taking account of the indications of the sensitive levels, heights may be measured accurately to within 0.002 mm. To eliminate the uncertainty in the correction for the refraction of light through the glass at the place where the point is under observation, and that in the correction for the temperature of the equilibrating mercury columns (as the capillary depression is only 0.01 mm. the uncertainty in it may be neglected) the tap $K\vartheta_0$ is introduced, and the spherical vessel d_5 forms part of the dead space [1]). If $K\vartheta_0$ is closed, and the mercury that stood in the narrow stem d_4 while the thermometer was being adjusted with $K\vartheta_6$ closed, is allowed to sink, there remains in the dead space only a very small and definitely known fraction of the total pressure, and the adjusting tube of the manometer must be lowered so as to bring the mercury levels once more to the two points. The displacement is read on a finely divided scale attached to the adjusting tube of the manometer, and at once gives in mm. of mercury the thermometer pressure for the temperature of the adjusting space, to which the only correction to be applied is that for the pressure remaining over.

We need not stop to describe the different devices (cf. Comm. No. 60, June 1900) by means of which the various points to be seen are so arranged that they can be brought in succession in sharp focus into the field of the cathetometer; the significance of the air-traps in the mercury filled connecting tubes is sufficiently obvious from the figure, as is also that of the mercury filled rubber tube *Sa* surrounding the rubber connecting tube S and its junctions with the other tubes. On account of the comparatively large value of viscosity, equilibrium is, in general, reached but very slowly between spaces occupied by gas at such low pressures as those obtaining in our thermometer reservoir and in the dead space. In the present instance, however, the favourable circumstance arises that only a very small quantity of gas has to flow over, seeing that the dead space is extremely small. Against the widening of the capillary it may be urged that then the quantity of gas contained in it would lead to inaccuracy owing to the uncertainty existing regarding the distribution of temperature along it. After full consideration of the change of viscosity and density with temperature, and also of constructional difficulties, the low temperature portion of the capillary was made of 37 cm. steel capillary of 0.5 mm. bore, and the part that is at practically room temperature was made of 50 cm. copper capillary of 1.0 mm. bore. The resulting uncertainty is, then, at the most, 1 %, while the viscosity is not yet excessive, seeing that it is possible to adjust to 0.01 mm. within a period of 2 minutes.

§ 3. *Densimetric Apparatus.* The part of the dilatometer that was immersed in the helium bath consisted of a reservoir Δ_1

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[1]) A coupling is inserted in the capillary d_2 by means of which many operations and controls are much more easily accomplished; it allows the whole manometer part of the arrangement to be loosened, and either that or the remaining apparatus may be connected independently with an air-pump, etc.

with a stem Δ_2, a narrow glass capillary Δ_3 continued by a steel capillary. The mass of helium here present was determined volumetrically in the bulb V_1 with a graduated stem both above and below, whose temperature was determined by that of the surrounding water bath; the pressure was read on a scale by using the branch V_{2b} of the mercury reservoir V_2. The dimensions of Δ_1 and V_1 are so chosen that the position of the mercury for the desired pressure can be read on the lower part of V_1's graduated stem before the dilatometer has been filled, and on the upper part after the filling has taken place. Moreover, the cross-section of the graduated stem has been chosen of such a size that when the dilatometer has been cooled again with $K_{\Delta v}$ and $K_{\Delta w}$ closed, after filling it at the boiling point to above the mark, the meniscus still remains in the stem even at the greatest densities employed.

Although the capillary is very narrow at the part where its temperature is uncertain, the correction for the gas condensed from it when the dilatometer is cooled (keeping $K_{\Delta v}$ and $K_{\Delta w}$ closed), which operates so as to cause a rise of the liquid meniscus in the stem, is of great importance when the question arises as to whether a maximum density can be shown to exist for helium or not. A second apparatus is therefore introduced having a very short stem and a similar capillary, but without a reservoir; to this the volumenometer W belongs. When the correction for the capillary of this control apparatus is calculated in exactly the same way as for the capillary of the dilatometer, it shows a rise of the level of the liquid that appears in the tube, and by comparing this with the observed rise one can obtain an indication of the accuracy of the correction.

For vapour density determinations the same dilatometer Δ_1 was used but along with the volumenometer Q; in this the gas was measured in a graduated tube, while it could be connected with Δ through $K_{\Delta Q}$ keeping $K_{\Delta v}$ closed.

§ 4. *Vapour Pressures of Helium.* The observed pressures have been corrected for the height of the helium surface above the middle of the thermometer reservoir $Th1'$, for the aerostatical pressure between the place where the pressure is measured and the surface of the liquid helium, and for the reduction of pressure due to friction along the coils of the regenerator spiral In this way the following values were obtained:

Helium, maximum pressure.

Temperature.			$760\ p_{\text{coëx.}}$
I.	II	mean.	
4°.29 K	4°.28 K.	4°.29 K.	760
3.97			565
3.26	3.20	3.23	197
2.34	2.40	2.37	51
1.47	1 49	1.48	3

See for correction Comm 124. p 15: note

Columns I and II refer to two independent measurements.

In fig. 1 of Pl. III $log\ p \times 760$ (where p is expressed in atmospheres) is graphed as a function of $\frac{1}{T}$. At the same time the figure gives us an idea of the agreement with the VAN DER WAALS vapour pressure law $log \frac{p}{p_k} = f\left(1 - \frac{T_k}{T}\right)$ from which it would follow that the curve should be a straight line.

The curvature of the experimental curve is but small, but it is still clear that f decreases at the lower temperatures.

If f is calculated from the tangent at $T = 4°.29$ K. it is found that $f = 1.2$, $T_k = 5°.8$ K., while the two temperatures 4°.29 and 3°.23 give $f = 1.1$, $T_k = 5°.7$ K. At lower temperatures f becomes still smaller, and the mean value would be found to be only $f = 0.9$, from which it would follow that $T_k = 6°.4$, a value that, considering the temperature of the BOYLE point, must certainly be too high.

It is worth remarking that this value of f differs very much from the values, ranging from 2 to 3, that have been found for ordinary normal substances¹). Helium, then, shows in a greatly exaggerated form the deviation from the mean $f = 2.7$ for ordinary normal substances that is already noticeable in the case of substances whose critical temperature lies below 0° C. which give a value $f = 2.2$. Associative substances deviate in the opposite direction; for instance, for water $f = 3.26$ and for isobutyl alcohol $f = 4.17$.

The new light now thrown upon the vapour pressure law for helium also allows a new estimate of the lowest temperatures that were reached in the experiments published in the VAN BEMMELEN Jubilee book, which were then estimated upon a basis of $f = 2.2$. With the value now obtained, the temperature for a vapour pressure of 1 mm. should be 1°.33 K., and for 0.15 mm., which was the lowest pressure reached, the temperature should be 1°.15 K., while, to reach a temperature of 1° K., the vapour pressure would have to be lowered to 1/25 mm.

§ 5a *Densities of Liquid Helium.* In the following table containing the experimental results, densities are expressed in terms of the normal density of the gas.

Helium, liquid densities.

T	$\frac{1}{v_{A\,liq}}$			
	I.	II.	III.	readjusted.
4° 33 K.	[658 0]			678.0
4°.29		682.3		682.3
4° 28			683.6	683.6
3°.98		715.5		715.5
3° 26		779.0		782.0
3.°20	784 8		785.9	785.9
2°.40	822 6		818.8	818.8
2° 34		815.4		820.0
1° 49			815.3	815.3
1° 47		810.9		815.0

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[1] KUENEN, Zustandsgleichung p. 142.

From these values ρ_{liq} is obtained by multiplying by $\rho_{0^\circ\,C.\ 760\,mm.} = 0.0001787$, so that we now get $\rho_{liq\ coëx\ 4^\circ.29} = 0.122$, where the roughly approximate value 0.15 was given before.

The great decrease in the expansibility as the temperature is lowered is remarkable. In the experiments of 1909 described in Comm. N⁰. 112 the impression had already been created that this would prove to be the case; the density values then obtained are given in column I. The results are shown graphically in fig. 2, Pl. III, and it is particularly noteworthy that there seems to be a maximum in the density; from the figure this seems to be at about 2°.2 K. Furthermore, it was clearly observed that, when the temperature was being lowered and passed 2° 1 K., the meniscus in the stem of the dilatometer became stationary, and rose again as the temperature sank further to 1°.48 K., while the reverse phenomenon was observed as the temperature rose again from this point to 2°.37 K. The following results show that the meniscus really stands lower in the stem at 2°.37 K. than at 1°.48 K. and that this is not due to the influence of condensation of gas from the dilatometer stem.

First experiment.

Temperature.	Position of the meniscus.		mean	
1°.47 K.			0.72	
2°.34	before cooling	0.52		
	after cooling	0.49	0.505	
		difference	0.215	
		correction	0.06	difference 0.155

Second experiment.

Temperature.	Position of the meniscus.		mean	
1°.49		0.59		
		0.58	0.587	
		0.59		
2°.40		0.42		
		0.37	0.393	
		0.39		
	observed minimum	0.35		
		difference	0.194	
		correction	0.082	difference 0.112

An idea of the accuracy of the corrections applied in each case may be got from the fact that, in the second experiment, the control dilatometer showed a rise of the meniscus of 0.03 as the temperature fell, while the calculated value was 0.028 The mean number 0.134 that remains after the correction has been applied, must be ascribed to expansion between 2°.37 K. and 1°.48 K. As far as a conclusion could be drawn from the observation, a maximum density point for helium has to be accepted. From a single observation in which the vapour pressure of the bath was lowered to 1 mm. it would have followed that no further expansion occurs as the temperature is lowered still more; but, in the meantime, this one observation, during which the bath was not stirred, is too uncertain to allow a definite conclusion as to whether or not the density of helium after attaining a maximum decreases till it reaches an invariable value.

§ 5b *Vapour Densities of Helium.* The density at a pressure of 65.54 cm. and a temperature of 4°.29 K. was found to be 69.0 times the normal density. Calculating B from the equation $pv - RT = B/v$, we get $B = -0.000047$; and, for the density of the saturated vapour at a pressure of 76 cm. a value of 85.5 times the normal. The correction for C to be applied according to the mean reduced equation of state VII. 1, although undoubtedly appreciable, appears to be too uncertain At 3°.23 K. by extrapolating values of the individual B's deduced from the helium isotherms between 0° and — 216°.56 C. (Comm. N^o^. 102*a*, Dec. 1907) B was found to be -0.000061, and this gives at 3°.23 K. a saturated vapour density 24.5 times the normal.

From these values various characteristic thermal data may be calculated for helium. If we deduce the slope of the MATHIAS diameter from 4°.29 K. and 3°.23 K. we find $-b_d = 0.0033$, and, taking the critical temperature to be 5°.5 K. and hence reaching the value $\rho_{kd} = 0.065$ we get for the constant of the MATHIAS diameter $-\mathfrak{b}_d = 0.255$. MATHIAS foretold that the value of $-\mathfrak{b}_d$ would be small, and he suspected that it would be 0.14. The first part of his remarkable prophecy is, therefore, hereby fulfilled.

For the critical virial ratio $K_4 = \dfrac{RT_k}{p_k v_k}$ we get (taking $T_k = 5°.5$ K., and $p_k = 2.75$) from ρ_{kd} a value 2.68, which is almost exactly the theoretical value deduced from the VAN DER WAALS equation of state. The value of this constant is thus markedly smaller for helium than for all other substances, with the exception of hydrogen, in which case it can be obtained only from very uncertain calculation yielding the result 2.9. (See KUENEN l. c. p. 60). The smallest known value is the one recently obtained for oxygen by E. MATHIAS and H. KAMERLINGH ONNES viz. 3.43. (Comm. N^o^. 117, June 1910). In a paper that will soon be published by C. A. CROMMELIN and H. KAMERLINGH ONNES [1]) a deduction from the isotherms of $K_4 = 3.28$ for argon will be given

§ 6. *Molecular Attraction in Helium.* The occurrence of a maximum density in a substance of such simple constitution as helium gives rise to questions of great import from the point of view of molecular theory. With a substance like water it is easy to imagine a particular molecular combination by which some of the parts are more closely united, while others are separated, the whole leading to an increase of volume as the temperature is lowered, and this especially when one considers that the dielectric properties of water probably play a part in the phenomenon. But helium atoms we are forced to consider as spherical and smooth, and, as appears from the ZEEMAN effect for helium, of the simplest possible internal construction; and for their case we seek in the meantime in vain for a basis for a similar explanation. Moreover, helium differs from ordinary normal substances, but in exactly the opposite way to that in which associated substances differ from them.

A dissociation increasing as the temperature is diminished, leading to an increase of the number of molecules (and, therefore of R in the equation of state), which would account for this deviation in the opposite sense, can scarcely be imagined. Should it appear that the change was occasioned by an increase in the dimensions of the helium atoms (that is, of b in the equation of state) as the temperature is lowered, then this, too, would be something strikingly unusual. The behaviour of helium seems rather to

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[1]) Comm. N^o^. 120*a*, Proceedings of this Meeting.

make it clear that even in the case of ordinary normal substances two different kinds of molecular attraction must be distinguished from each other — an attraction of comparatively large sphere of action, and an attraction that is local, but more intense, of smaller range, and confined to the immediate neighbourhood of the surface of the molecule; this latter attraction causes ordinary normal substances when compared with helium to resemble rather associative substances; in the case of liquid helium the latter type of action of the attraction would, then, be suppressed.

If it is not, indeed, entirely absent in helium, the sphere of influence of this force must have wholly withdrawn within the space occupied by the atom at the lowest temperatures (which is probably also to a large extent the case for substances like hydrogen at the lowest temperatures at least); and, therefore, the predominance of characteristics which are just the reverse of those in associative substances leads to the supposition that in our case a part of the attraction diminishes with the temperature. Even this idea is at first sight strange, for we are familiar with the idea of attraction increasing as temperature falls. According to Boltzmann's law this increase must take place in a perfectly definite manner, even for a constant attraction between the molecules. When, therefore, we assume a decrease in the cohesion this must exist notwithstanding the cause for increase given by Boltzmann's law. It would, perhaps, be due to the fact, that at lower temperatures the decrease in the attractive force originating in the helium atom would predominate.

Let us work out a little further a modification that will affect the behaviour of the substance in such a way as to decrease the attraction, the a of van der Waals, with the temperature decreasing below a certain temperature. Its importance is far more radical than that which occasions an increase, for, while the latter changes the phenomenon more in degree, the former can occasion a fundamental alteration.

A few simple illustrations may illustrate this point. For the sake of simplicity let us take the van der Waals equation of state. Putting a and b constant for higher temperatures so that T_k can be calculated, and putting also the attraction $a = KT$ from $T = 0$ to $T = T_\mathrm{k}$ and, therefore $a = KT_\mathrm{k}$ at T_k, it follows

then, in such a simple manner that it is not necessary to write down the equations here, that all temperatures below the critical T_k show the critical phenomena for $v = 3b$, the critical pressure being for every temperature proportional to the absolute temperature, viz. $\frac{1}{27}\,\frac{KT}{b^2}$. With respect to the individual isotherms, the gas above T_k behaves as a van der Waals substance, in correspondence with our assumption $a = \mathit{const.}$, but, for every temperature T below T_k, the isotherms are determined by taking the isotherm of T_k and shortening its ordinate in the ratio of T to T_k.

Assuming now that $a = KT$ holds only up to a certain temperature $T_1 < T_\mathrm{k}$, and that $a = \mathit{const.}$ is the law from $T > T_1$ onwards, then the isotherms from the critical temperature to T_1 are determined from the equation of van der Waals, and from this equation, too, are determined the maximum vapour pressure, and liquid and vapour densities. Isotherms for lower temperatures are then determined from these by taking the ordinates for each volume from the isotherm for T_1 and diminishing it in ratio of T to T_1. The densities of coexisting liquid and vapour phases would thus remain unaltered, while their common pressure would be simply proportional to T. Although with helium the maximum vapour pressure diminishes less rapidly with the temperature than is the case with ordinary normal substances, the diminution is still very much greater in reality than would be the case under the conditions above assumed.

A substance that fulfilled these conditions would, moreover, exhibit some other very unusual properties. The energy change at constant temperature would be zero, the latent heat of vaporization would alone be necessary for external work, and so the internal latent heat of vaporization would be zero.

To realise the significance of the modifications which the thermodynamical properties of a substance undergo when the molecular attraction decreases with the temperature, let us assume that it decreases more rapidly than in simple ratio; in that case one is brought to the deduction of still stranger properties. We may here mention the case in which $a = cT^2$ for temperatures below $T_1 < T_\mathrm{k}$. With such a substance at a temperature beneath T_1, lowering of the temperature would diminish the difference between the liquid and vapour densities, and this difference would disappear at a temperature T_{ki} determined from the conditions $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv^2} = 0$ by the equation $T_{ki}\, T_k = T_1{}^2$. Hence, an *inferior critical point* occurs from which to the absolute zero the substance once more behaves as a perfect gas. For this case the change of energy with volume is negative, and so too is, therefore, the internal latent heat.

We have still to examine if there are further assumptions which are consistent with a decrease in the molecular attraction as the absolute zero is approached.

The nearest comes in this respect KELVIN's and J. J. THOMSON's idea of the structure of atoms. Assume, for example, that an atom consists of a sphere of uniformly distributed positive electricity inside which is an electron; then two such atoms would, at the absolute zero where the electron comes to rest, exert no electrical attraction upon each other. As soon, however, as the electrons begin to oscillate about their positions of equilibrium, and begin to describe orbits about their centres, attraction begins to be felt. An investigation similar to those made by VAN DER WAALS JR. based upon the principles of statistical mechanics would be necessary before one could say how the molecular attraction of a system of such atoms would depend upon the effects of collisions and of temperature radiation (they are, in fact, vibrators such as those assumed by PLANCK and EINSTEIN). *A priori*, it seems to be not impossible that a increases over a definite temperature region as the temperature rises.

In the meantime all these theories do no more than emphasise the fact that the behaviour of helium forces us to question the significance of the absolute zero with respect to molecular attraction. Hence it is of first consequence to obtain data concerning the thermal properties here mentioned in connection with helium that would lead to the solution of these problems, and also to investigate related properties such as capillarity, viscosity, specific heat, refractive index and dielectric constant, for which data are still lacking. For this purpose the solution of the problem of transferring liquid helium to a vessel in which the regenerator

spiral no longer interferes with the introduction of measuring apparatus is absolutely essential.

B. *On the change in the resistance of pure metals at very low temperatures, etc.* III. *The resistance of platinum at helium temperatures.*

§ 1. *The resistance of a wire of very pure platinum at helium temperatures.* As soon as the possibility had been attained, it lay at hand to extend to helium temperatures the investigation of the change of electrical resistance of pure metals that, in Comm. No. 99*c* (June 1907), had been brought down to the lowest hydrogen temperatures. For this purpose the resistance Pt_B which had been calibrated at hydrogen temperatures as well as at others with the resistance Pt_I of Comm. No. 99*b* (June 1907) was available It was constructed on the model of Pt_d (Comm. No. 99*b* § 2), and is indicated by Ω on Plate I of part *A* of the present paper, fig. 1. The thin platinum wire is wound round a glass cylinder and is kept tight on it by being wound while hot, and the thicker platinum ends W_a and W_b are fused to the glass. To these ends the double platinum leads W_{a_1}, W_{a_2} and W_{b_1}, W_{b_2} are attached; they are not, however, welded in the blowpipe, but are simply tin-soldered. The resistance was measured on the WEATSTONE bridge according to the method described in Comm. No. 99 and previous Communications. The ratios of w_t, the resistance at the temperature of the observation, to w_0, that at 0° C., are here given.

Resistance of platinum wire Pt_B	
T	$\frac{w_t}{w_0}$
273°.09 K.	1
20.2	0.0171
14.2	0.0135
4.3	0.0119
2.3	0.0119
1.5	0.0119

From this it appears that by descending to helium temperatures the resistance is still further diminished, but when these temperatures are reached the resistance attains a constant value quite independent of the individual temperature to which it has been brought. The results are plotted in fig. 3 Pl. III, which shows well the asymptotical approach of the resistance to a constant value at 4°.3 K.

§ 2. *The probable resistance of pure platinum and of pure gold at helium temperatures.* In order to establish the exact significance of the result just obtained we must take account of the fact that the wire Pt_B was not made from quite pure metal, and we must allow for the probable influence of this difference from pure platinum.

With this end in view, we shall first confine our attention to the observations that have been made upon gold (Comm. N⁰. 99). Remembering the close resemblance between the differences of the resistances of platinum and of gold wires from a linear function of the temperature, we may, in view of the result that has been obtained with platinum, extrapolate the Au_V resistance curve to give a constant value at helium temperatures. This has been done in fig. 3 of Plate III. The parts of the curves obtained from observations are drawn with thicker lines. We now note that, according to § 1 of Comm. N⁰. 99*c* by KAMERLINGH ONNES and CLAY (June 1907) the influence of admixtures can be represented with rough approximation even down to hydrogen temperatures by an additive resistance that is independent of the temperature. In this way the line correspondingly marked in the figure was obtained for Au_{III} which was constructed of gold of a smaller degree of purity (0.015 % admixture against 0.005 % for Au_V). According, now, to § 1 of Comm. N⁰. 99*c* the effect of admixture should be pretty well proportional to the quantity present, and this would lead to negative values for pure gold. In the first place, however, we do not know if the impurity was the same in the two cases, nor do we know the influence of possible tensions in the metal; but moreover, such great uncertainty exists in our rough approximations as to confine our most probable result in the meantime to this: That within the limits of experimental error (the degree of purity attainable) the resistance of pure gold is already zero at helium temperatures.

Let us return to platinum. The wire Pt_B seems to be less pure than Pt_I (see table V of Comm. N⁰. 99*b*), and, moreover, the fixing of the wire on the glass may give rise to undesirable effects. By putting the additive resistance once more constant, to a first approximation, extrapolation gives for Pt_I the corresponding line shown in the graph But still, the resistance of Pt_I may not without further comment be regarded as the resistance of pure platinum. A wire of greater diameter used by HOLBORN gave a greater relative decrease of the resistance from 0° to — 191° C. If we extrapolate these values to lower temperatures the resistance remaining at helium temperatures, and independent of any further change of temperature, would be nearer zero. One may ask if it is not possible to put the difference between the two wires obtained from HERAEUS inversely proportional to the thickness and in that way deduce a value for pure platinum unaffected by the individual treatment of each; but this method would lead us too far into the region of pure conjecture. But still, the conclusion seems to be fully established that the resistance of pure platinum is, within the limits of experimental error — the attainable degree of purity — already zero at helium temperatures.

§ 3. *The change with temperature of the resistance of pure metals at low temperatures.* I was formerly of the opinion that the resistance of pure metals reaches a minimum as the temperature is diminished, and then, as the temperature sinks still further, again begins to increase and becomes infinitely great at the absolute zero; but now it seems to me to be more probable that, even before the absolute zero is actually reached, the resistance if not zero, has become so extremely small that it practically vanishes, and that this remains the case for further lowering of the temperature.

In view of this result, then, we must also abandon the theory that has served for years as a guide in our Leiden researches upon the resistance of metals at low temperatures, according to which it was imagined that the resistance would attain a minimum as the temperature was lowered and would become infinitely great at $T = 0$, in consequence of the assumption that the electrons which are the actual conductors in metals would, as was expressed by me in 1904, begin to precipitate on the atoms as a vapour on being cooled to hydrogen temperatures, or as **Koenigsberger** — in a manner leading to a similar dependence upon temperature — explains the phenomenon that was then supposed to exist, by the recombination of the electrons that had been freed by dissociation. I already questioned the validity of this assumption with respect to its application to perfectly pure metals at hydrogen temperatures, when the latest experimental results (Comm. by **Kamerlingh Onnes** and **Clay**) obtained with extremely pure gold showed that the point of proportionality would always have to be sought at still lower temperatures. It is now quite clear that in the case of metals like gold and platinum at any rate that theory must be dropped. It seems that the free electrons in the main remain free, and it seems to be the movable parts of the vibrators that are now bound, their motion at ordinary temperature forming the obstacles to conduction; these disappear when the temperature is lowered sufficiently as the vibrators become practically immovable [1]. There is, in the meantime, no occasion to calculate, unless for still much lower temperatures which cannot just yet be realised, a "latent heat of vaporization" or a "dissociation constant" for the electrons for the case of pure metals of the type treated.

The marked decrease in the resistance until it becomes practically zero at a temperature just above 4°K. and its remaining at this value as the temperature is lowered further as has been shown over a range of about two and a half degrees, so that, as far as resistance of these metals is concerned, the boiling point of helium is practically the absolute zero, points in another direction. It seems to me to be connected with the change with temperature of the heat energy of molecular motion of solid substances that has been deduced by **Einstein** in his theory of the specific heats, on the assumption that it is the energy of vibrators determined by radiation equilibrium.

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[1] That the vibrators become practically immovable represents what we have formerly called the "freezing" of the electrons.

In particular an obvious assumption to make is that the mean free path of the electrons which provide conduction is determined by the elongation of the above mentioned vibrators. To further illustrate this point let us keep as closely as possible to the theory of electrical resistance of **Riecke** [1], **Drude** and **Lorentz**, who has developed it into a pure theory of electrons. We take the formula

$$\gamma = \frac{1}{3}\frac{\varepsilon^2}{c^2}\frac{NL\mathfrak{g}}{\alpha T}$$

where γ is the electrical conductivity of a cube of unit volume, N the density of the free electrons, L their mean free path, $\mathfrak{g}$ their molecular speed, and c the speed of light, ε the elementary charge and $\alpha\ T$ the kinetic energy of a free electron while T is the absolute temperature. Putting $p = \frac{1}{3}\frac{\varepsilon^2}{C^2\alpha}\frac{\mathfrak{g}}{\sqrt{T}}$, this becomes c

$$\gamma = \frac{pNL}{\sqrt{T}}$$

and according to **Riecke** if $q = \frac{\mathfrak{a}\sqrt{T_s}}{\pi(1+\beta s)^2}$, where $\mathfrak{a}$ is the distance between the atoms supposed te be cubically arranged, s the ordinary and T_s the absolute temperature of the melting point, β in **Riecke**'s notation the coefficient of linear expansion, $L = \frac{q}{\sqrt{T}}$. Instead of this hypothesis of **Riecke**'s we shall put $L = \frac{q'}{\sqrt{E_T}}$

in which
$$E_T = 3R\frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}$$

where $\beta = 4.864 \times 10^{-11}$, now represents, according to **Planck**, the energy of a vibrator whose frequency is ν. The product $\beta\nu$ we will call as usually is done a.

We then get for the ratio of the conductivity γ_T at any temperature T, to γ_0 that at 0° C. the value

$$\frac{\gamma_T}{\gamma_0} = \frac{\sqrt{T_{0°C.}E_{0°C}}}{\sqrt{TE_T}}.$$

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[1] **Riecke**, Physik. ZS. 1909, p. 512.

This formula gives, in fact, good expression to the decrease with temperature of the resistance of pure metals of the kind here considered (monatomic ?). It shows in the first place the decrease to zero at a temperature above the absolute zero. For $\beta\nu = a = 54$ the resistance at helium temperatures becomes about 0.0001 times that at 0° C.

If we may further assume that $\frac{a}{T}$ is already small at 0°C., then the resistance w_T at T in terms of the resistance w_0 at 0°C. becomes

$$\frac{w_T}{w_0} = \frac{T - \frac{1}{4}a}{273.1 - \frac{1}{4}a}.$$

In fact, at 0°C. the temperature coefficients of the resistances of pure metals are, as a rule, greater than 0.00367, and, for platinum, gold, silver and lead they lie in the neighbourhood of 0.0039 and 0.0040.

And lastly, the formula also expresses well the fact that the diminution of resistance diminishes in quantity at hydrogen temperatures, and that in greater degree for substances of high melting point than for those of low melting point.

An accurate numerical equation, however, such as to determine even the bend in the curve that represents the resistance as a function of the temperature can be obtained only on the assumption that smaller values of ν and, therefore, of a come in the front at lower temperatures. Definite values, indeed, cannot be ascribed to ν. Einstein [1]), for instance, deduces from its elasticity $a = 200$ for silver (for he gives $\lambda = 73.10^{-4}$ cm. for the wave-length in vacuum corresponding to ν), while Nernst [2]) from the specific heat, deduces the value $a = 162$ corresponding to $\lambda = 90.10^{-4}$, a number, however, which is not of itself sufficient to represent

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[1]) A. Einstein. Ann. d. Phys. (4) 34 (1911) p. 170. Since the address delivered in the December meeting was only ready for printing in the number of the Dutch Proceedings for Febr. 1911 I have been able to add then the following calculations from the elasticity to what I communicated in December.

[2]) Cf. also Madelung, Gött. Nach. 1909, p. 100, who was the first to calculate the period of molecular vibrations.

the wole behaviour of silver. For lead, Nernst gives $a = 58$, while Einstein gets $a = 108$ from the elasticity. Moreover, according to the elasticity a should increase somewhat at lower temperatures, while, from the specific heat, it would appear that the change should take place in the same sense as that in which the resistance changes. This, too, shows that the theory is still far from perfect.

As there exists so much uncertainty, and as it is more a question of showing that the introduction of vibrators leads to a qualitative explanation of the sense in which the observed change of resistance deviates from proportionality to temperature, I have taken for a one half of each of the values obtained by Einstein from the elasticity. In this way we obtain for a:

for Pt 111, Ag 100, Au 92, Pb 54.

T	$\frac{T}{273.1}$	$\frac{w_T}{w_0}$ platinum		silver		gold		lead	
		C	O	C	O	C	O	C	O
372°.86	1.365	1.405		1.401	1.411	1.397		1.384	
273.1	1	1	1	1	1	1	1	1	1
169.29	0.617	0.579	0.581	0.583	0.581	0.586	0.593	0.601	0.594
77.93	0.285	0.213	0.199	0.220	0.197	0.225	0.219	0.250	0.253
20.18	0.074	0.012	0.014	0.015	0.009	0.018	0.008	0.035	0.030
13.88	0.054	0.003	0.010	0.004	0.007	0.005	0.003	0.015	0.012
4.30	0.016	0.000	[0.009]	0.000		0.000	[0.002]	0.000	

It appears, therefore, that there is indeed a qualitative correspondence [1]). Before we can attach any greater importance to it,

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[1]) The numbers are all taken from the Leiden observations (Kamerlingh Onnes and Clay l. c.) and they refer to the purest of the wires, while the probable negative correction for the influence of admixture and for the results of treatment during manufacture necessary for its expression in terms of the pure metal have been omitted. The influence of admixture is such as to give rise to impediments distributed, at distances determined by the quantity of admixture present, throughout the metal, which exert an influence

however, it would have to be shown that the ratio of heat conductivity to electrical conductivity at hydrogen temperatures [1]) satisfies the conditions imposed by RIECKE's modified theory [2]).

At all events in developing new theoretical considerations it seems desirable to take into account the result obtained [3]).

I gratefully record my indebtedness to Dr. C. DORSMAN for his intelligent assistance during the whole of this investigation, and to Mr. G. HOLST, who conducted the measurements with the WHEATSTONE-bridge with much care

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upon the mean free path of the free electrons, that is proportional to $\sqrt{T}$ and therefore an influence on the resistance that is independent of the temperature, just as mixed crystals do in alloys.

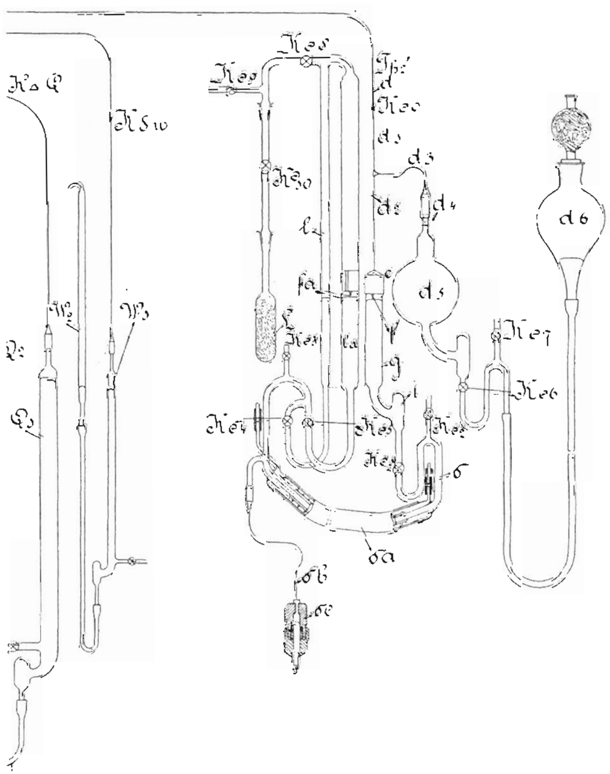
Estimating for mercury $a = 30$ on account of its lower melting-point, we get the following multiples of the value extrapolated to 0° C. from observations on the solid state (loc. cit.).

$T =$	77°.93 K.	20°.18 K.	13°.88 K.
calculated	0.263	0.050	0.027
observed	0.279	0.056	0.033

[1]) Experiments to elucidate this point have been in preparation for some time.

[2]) An assumption that may obviously be made is that the energy of the vibrators determines the increase of volume from the absolute zero, with which the explanation of the relation between expansion and change of resistance on one hand, and between expansion coefficient and specific heat on the other hand, deserves to find a place in the theory.

[3]) The further question calls for attention that is suggested by it regarding the peculiarities of the motion of electrons through conductors when, by taking all precautions, the mean free paths are as large as must, in the meantime, be assumed that they can be made (and begin to be comparable with the thickness of very thin layers).



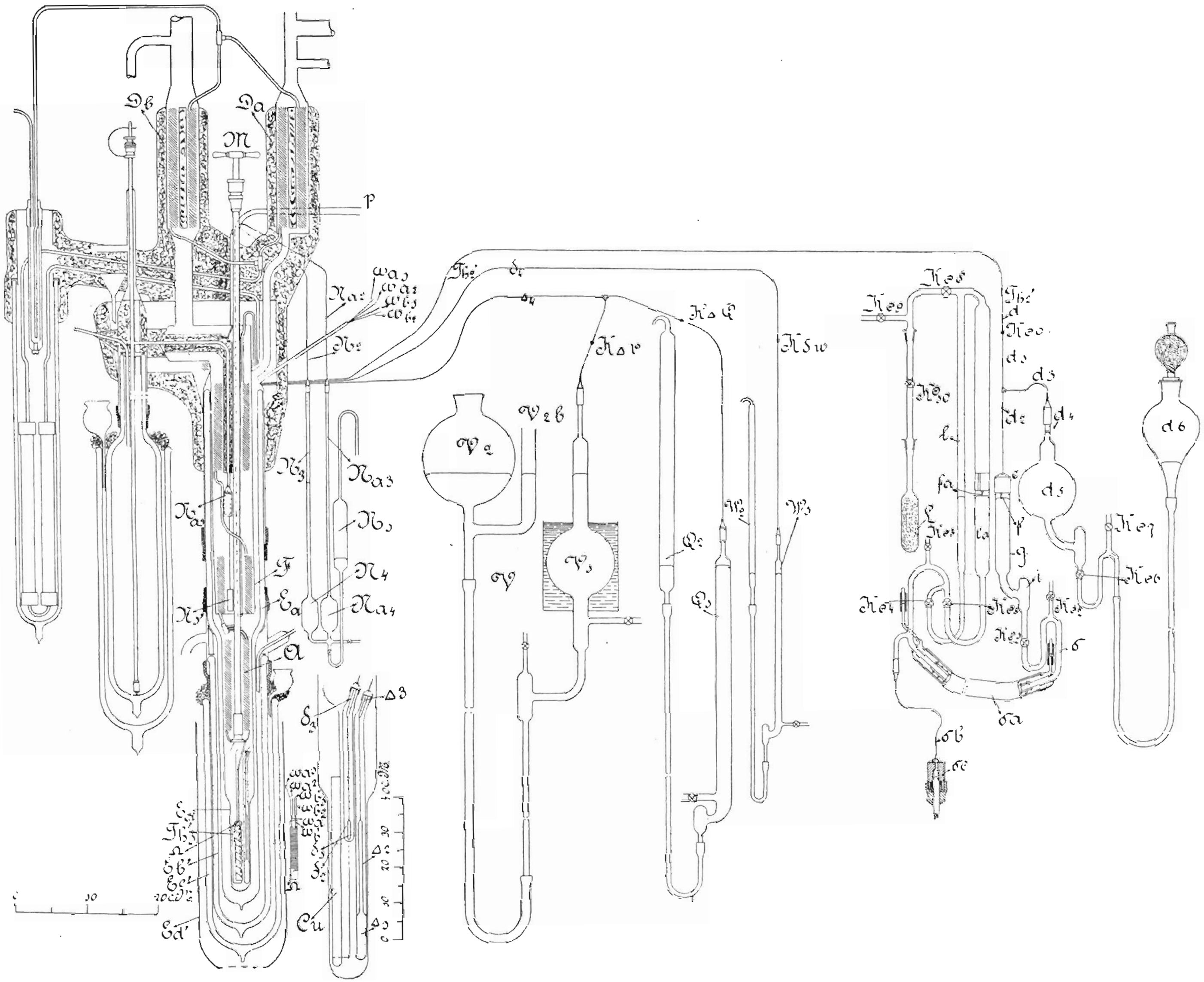


Fig. 1.   Fig. 2.

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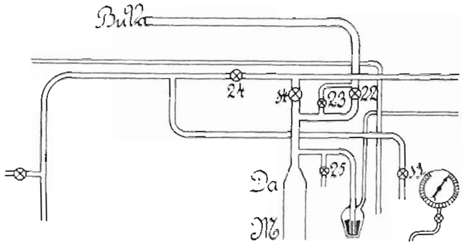

Fig. 1

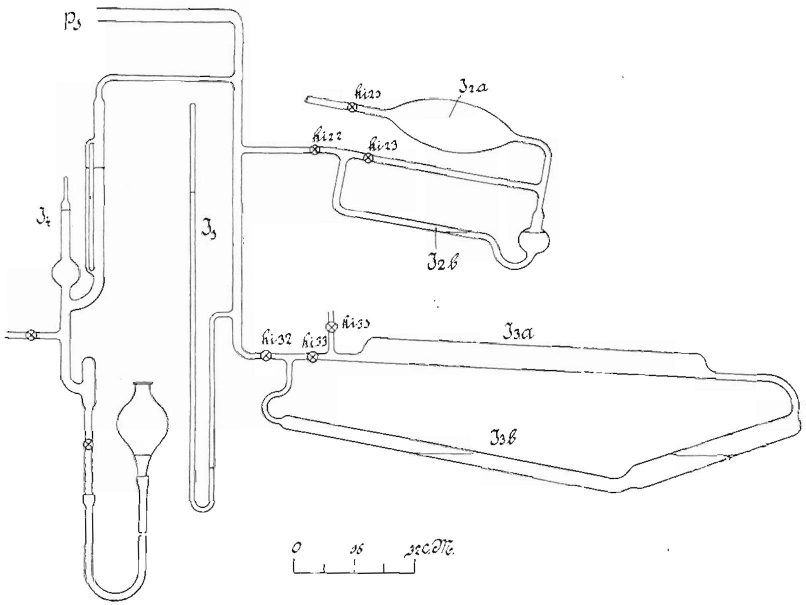

Fig. 2.

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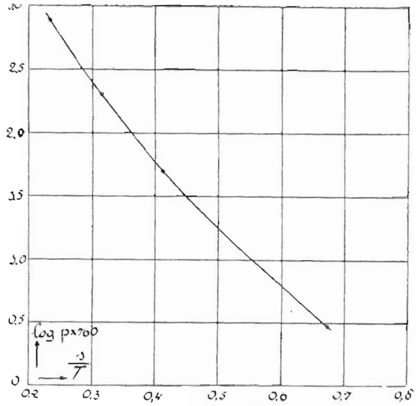

Fig. 1. Vapour pressure of helium.

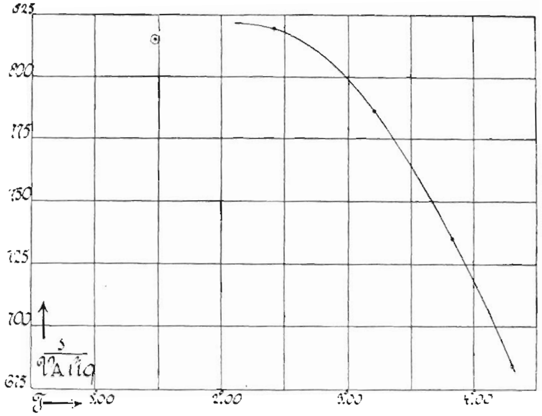

Fig. 2. Densities of liquid helium.

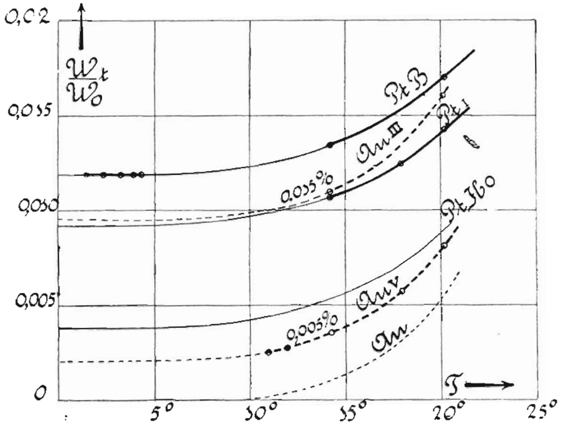

Fig. 3. Resistances of platinum.