

Citation:

H. Kamerlingh Onnes, The liquefaction of helium., in:
KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 168-185

The lefthand part agrees then perfectly with BAKHUIS ROOZEBOOM's spacial figure, O_A and O_B not representing the melting-points under vapour-pressure, but the transition points of the two components under vapour pressure, i. e. the points where the ordinary crystalline state passes to the fluid crystalline state under the pressure of its vapour.

If this spacial figure is cut by a plane of constant pressure, we get, at least if this pressure is chosen high enough, the simplest imaginable T - X -figure of a system of two components, each of which possesses a stable fluid-crystalline modification.

The other possible cases may be easily derived from this spacial figure.

Amsterdam June 1908.

Anorg. Chem. Laboratorium
of the University.

Physics. — "*The liquefaction of helium*". By Prof. H. KAMERLINGH ONNES. Communication N°. 108 from the Physical Laboratory at Leiden.

§ 1. *Method.* As a first step on the road towards the liquefaction of helium the theory of VAN DER WAALS indicated the determination of its isotherms, particularly for the temperatures which are to be attained by means of liquid hydrogen. From the isotherms the critical quantities may be calculated, as VAN DER WAALS did in his Dissertation among others for the permanent gases of FARADAY, which had not yet been made liquid then, either by first determining a and b , or by applying the law of the corresponding states. Led by the considerations of Comm. N°. 23 (Jan. 1896)¹⁾ and by the aid of the critical quantities the conditions for the liquefaction of the examined gas may be found by starting from another gas with the same number of atoms in the molecule, which has been made liquid in a certain apparatus. By a corresponding process in an apparatus of the same form and of corresponding dimensions the examined gas may be made liquid.

¹⁾ [Developed in view of the statical liquefaction of hydrogen and the obtaining of a permanent bath of liquid hydrogen (Comm. N°. 94f) at which I was working then].

By [] will be designed additions made in the translation.

The JOULE-KELVIN effect, which plays such an important part in the liquefaction of gases whose critical temperature lies below the lowest temperature down to which we can permanently cool down, may be calculated from the isotherms, at least if the specific heat in the gas state is not unknown, and its determination, though more lengthy than that of the isotherms, may be an important test of our measurements. If there is to be question of statical liquefaction of the gas by means of the JOULE-KELVIN effect, this must at all events give a decrease of temperature at the lowest temperature already reached, which, as was demonstrated in the above communication, will be the case to a corresponding amount for gases with the same number of atoms¹⁾ in the molecule at corresponding states, while a mon-atomic gas compared with a di-atomic one will be in more favourable circumstances for liquefaction (Comp. also Comm. N°. 66, 1900).

But the sign of the JOULE-KELVIN effect under certain circumstances does not decide the question whether an experiment on the statical liquefaction of a gas will succeed. Speaking *theoretically*, when by the JOULE-KELVIN effect, at a certain temperature a decrease of temperature however slight can be effected, liquid may be obtained by an adiabatic process with a regenerator coil and expansion cock with preliminary cooling down of the gas to that temperature. But as long as we remain too near the point of inversion the JOULE-KELVIN effect will have a slight value; accordingly the processes by which really gas was liquefied in statical state with an apparatus of this kind, as those which were applied to air by LINDE and HAMPSON, and to hydrogen by DEWAR, start from a much lower reduced temperature, viz. from about half the reduced temperature at which the sign of the JOULE-KELVIN effect at small densities is reversed, or more accurately from somewhat below the BOYLE-point, i.e. that temperature at which the minimum of pv is found at very small densities. [Experiments from which could be derived at how much higher reduced temperature the process still succeeds with mon-atomic gases are lacking]. So according to the above theorem it is *practically* the question whether the lowest temperature at our disposal lies below this BOYLE-point²⁾

¹⁾ [The inversion points of the effect having reference to the amount 0 and therefore being independent of the number of atoms in the molecule, are at corresponding states, and the inversion point for small densities is at corresponding temperature for *all* gases as far as they obey the law of corresponding states. This is easily deduced from the considerations of Comm. N°. 23].

²⁾ [The BOYLE point, as well as the JOULE-KELVIN inversion point for small densities is a corresponding temperature and both temperatures are therefore proportional theoretically. In the present question it is better to refer to the BOYLE point than to the JOULE-KELVIN inversion point considering the deviations of the law of corresponding states].

which is to be calculated from the isotherms, and the JOULE-KELVIN effect has therefore a sufficient value to yield an appreciable quantity of liquid in a given apparatus in a definite time.

Three years ago I had so far advanced with the investigations which led to the isotherms of helium,¹⁾ that these determinations themselves could be taken up with a reasonable chance of success.

At first the great difficulty was how to obtain sufficient quantities of this gas. Fortunately the Office of Commercial Intelligence at Amsterdam under the direction of my brother, Mr. O. KAMERLINGH ONNES, to whom I here express my thanks, succeeded in finding in the monazite sand the most suitable commercial article as material for the preparation, and in affording me an opportunity to procure large quantities on favourable terms. The monazite sand being inexpensive, the preparation of pure helium in large quantities became chiefly a matter of perseverance and care.²⁾

The determination of isotherms of helium was not accomplished before 1907.

The results of the determinations of the isotherms were very surprising. They rendered it very probable that the JOULE-KELVIN effect might not only give a decided cooling at the melting point of hydrogen, but that this would even be considerable enough to make a LINDE-HAMPSON process succeed.

Before the determinations of the isotherms had been performed I had held a perfectly different opinion in consequence of the failure of OLZEWSKI's and DEWAR's attempts to make helium liquid, and had even seriously considered the possibility that the critical temperature of helium, might lie if not at the absolute zero-point, yet exceedingly low. In order to obtain also in this case the lower temperatures, which among others are necessary for continuing the determinations of isotherms below the temperatures obtainable with solid hydrogen, I had e.g. been engaged in designing a helium motor (cf. Comm. N°. 23) in which a vacuumglass was to move to and fro as a piston in another as a cylindre. And when compressed helium was observed to sink in liquid hydrogen (Comm. N°. 96, Nov. 1906) I have again easily suffered myself to be led astray to the erroneous supposition of a very low critical temperature.

In the meantime I had remained convinced that only the deter-

¹⁾ [Comp. for cryostats: Comm. Ns. 14, 51, 83, 94, for thermometry: Comm. Ns. 27, 60, 77, 93, 95, 99, 101, 102, for manometers, piezometers and determination of isotherms: Comm. Ns. 44, 50, 69, 70, 71, 78, 97, 99, 100].

²⁾ [Even the quantity of 200 liters (and 160 liters of reserve) of the extreme purity required, though requiring a great deal of labour, was not out of reach].

mination of the isotherms could decide how helium could be made liquid. Hence we had proceeded with what might conduce to making a favourable result for the critical temperature at once serviceable. Thus the preparation of a regenerator coil with expansion cock in vacuum glass (to be used at all events below the point of inversion), and the preparation of pure helium was continued. Of the latter a quantity had even been gradually collected sufficiently large to render a determination of the JOULE-KELVIN effect in an apparatus already put to the test in preliminary investigations possible, and to enable us to make efficient expansion experiments.

All at once all these preparations proved of the greatest importance when last year (Comm. N°. 102a) the isotherms began to indicate 5° K to 6° K for the critical temperature, an amount which according to later calculations, which will be treated in a subsequent paper, might have been put slightly higher (e.g. $0,5'$), and which was in harmony with the considerable increase of the absorption of helium by charcoal at hydrogen temperatures, on the strength of which DEWAR had estimated the critical temperature of helium at 8° K. For according to the above theorem it was no longer to be considered as impossible to make helium liquid by means of a regenerator coil, though this was at variance with the last experiments of OLSZEWSKI, who put the critical temperature below 2° .

It is true that the conclusions drawn from the isotherms left room for doubt. It seemed to me that the isotherms at the lowest temperature yielded a lower critical temperature than followed from the isotherms at the higher temperatures, which is due to peculiarities, which have been afterwards confirmed by the determination of new points on the isotherms. So there was ample room for fear that helium should deviate from the law of the corresponding states, and that still lower isotherms than those already determined should give a still lower critical temperature than 5° K., and according as the critical temperature passed on to lower temperatures the chance to make helium liquid by means of the JOULE-KELVIN effect beginning at the lowest temperatures to be reached with liquid hydrogen (solid hydrogen brings new complications with it) became less. This fear could not be removed by the expansion experiment which I made some months ago, and in which I had thought I perceived a slight liquid mist. (Comm. N°. 105 Postscriptum March 1908). For in the first place only an investigation made expressly for the purpose could decide whether the mist was distinct enough, and whether the traces of hydrogen the presence of which was still to be demonstrated spectroscopically, were slight enough to allow us to attach any im-

portance to the phenomenon. And in the second place the mist was very faint indeed, which might point to a lower critical temperature than had been derived.

So it remained a very exciting question what the critical temperature of helium would be. And in every direction in which after the determination of the isotherms in hand we might try to get more information about it, we were confronted by great difficulties.

As, however, they consisted in the arrangement of a cycle with cooled helium, [this being indispensable to integrate cooling effects with a reasonable quantity of helium] the labour spent for years on the arrangement of the Leiden cascade of cycles for accurate measurements, might contribute to the surmounting of them. Arrived at this point I resolved to make the reaching of the end of the road at once my purpose, and to try and effect the statical liquefaction of helium with a circulation, as much as possible "corresponding" to my hydrogen circulation.

In this I perfectly realized the difficulty to satisfy at the same time the different conditions for success [allowing for possible deviations from the law of corresponding states]. For [though the suitability of the hydrogen cycle for the cooling down of the compressed helium to 15° K. was amply proved (Comm. N°. 103)] the preliminary cooling to be reached was, as to the temperature, only just within the limit at which it could be efficient, nor were the other circumstances which could be realized, any more favourable.

Of course the scale on which the apparatus intended for the experiment in imitation of the apparatus which had proved effective for hydrogen, would be built, was not only chosen smaller in agreement with the value of b which was put lower, but taken as small as possible. That the reduction of HAMPSON's coil to smaller dimensions does not diminish its action had been found by former experiments, and has been very clearly proved by what OLSZEWSKI tells about the efficiency of his small hydrogen apparatus. I could not, however, reduce below a certain limit without meeting with construction problems, about which the hydrogen apparatus had not given any information. We had to be sure that the capillaries would not get stopped up, that the cocks would work perfectly, that the conduction of heat, friction etc. would not become troublesome. When in connection with the available material, the smallest scale at which I thought the apparatus still sufficiently trustworthy, reduction to half its size, had been fixed, the dimensions of the regenerator coil, though as small as those of OLSZEWSKI's coil, proved

still so large that the utmost was demanded of the dimensions of the necessary vacuum glasses; which was of the more importance, because the bursting of the vacuum glasses during the experiment would not only be a most unpleasant incident, but might at the same time annihilate the work of many months.

Besides the difficulties given by the helium liquefactor itself, the further arrangement of the cycle in which it was to be inserted, offered many more.

The gas was to be placed under high pressure by the compressor, and was to be circulated with great rapidity. Every contamination was to be avoided, and the spaces which were to be filled with gas under high pressure were to have such a small capacity, that they only held part of the available naturally restricted quantity of helium.

As compressor only CAILLETET's modified compressor could be used, a compressor with mercury piston, which had been arranged for experiments with pure and costly gases, and was described in Comm. N°. 14 (Dec. 1894) and Comm. N°. 54 (Jan. 1900), and which also served for the compression of the helium in the expansion experiments of last March (Comm. N°. 105)¹⁾.

That it could only be charged to 100 atms., a fact which I had sometimes considered as a drawback in the case of experiments with helium, could no longer be deemed a drawback after the determinations of isotherms had taught that even if the pressure of helium compressed above 100 atms. at low temperatures is raised much, the density of the gas increases but little. Accordingly I had not gone beyond 100 atms. in my expansion experiments. The higher pressures which DEWAR and OLSZEWSKI applied in their expansion experiments, have been a decided disadvantage, because they involved the use of a narrower expansion tube. With regard to the circulation now to be arranged, with estimation of the critical pressure at 7 or 5 atms.²⁾, according as b was put at a third or half that of hydrogen, a pressure of 100 atms. in the regenerator coil had to be considered as sufficient according to the law of corresponding states.

But for a long time it was considered an insuperable difficulty that the compressor conjugated to the auxiliary compressor could circulate at the utmost 1400 liters of gas measured at the ordinary

¹⁾ [Just as when it was used to get a permanent bath of liquid oxygen (completed 1894 Comm. N°. 14) it was now again in the pioneering cycle and rewarded well the work spent on it, especially in 1888 when I was working at the problem to pour off liquid oxygen in a vessel under atmospheric pressure by the help of the ethylene cycle].

²⁾ [The results of the isotherm of helium at -259° to be treated in a following communication were not yet available then; they point to a smaller value].

temperature per hour, $\frac{1}{16}$ of the displacement with the hydrogen circulation. Not before experiments with the latter had been made, in which the preliminary cooling of the hydrogen did not take place with air evaporating at the vacuum pump (so at -205°) but under ordinary pressure (so at -190°), and moreover the hydrogen compressor ran 4 times more slowly than usual, and in these experiments liquid hydrogen had yet been obtained, it might be assumed that the circulation process to be realized would still be sufficient to accumulate liquid helium.

With regard to the parts of the compressors, the auxiliary apparatus, and the conduits, which in the course of the experiment assume the same pressure as the regenerator coil, their joint capacity was small enough to enable us to make the experiment with a quantity of 200 liters. This quantity of pure helium besides a certain quantity [160 liters] kept in reserve could be ready within not too long a time¹⁾.

A great difficulty of an entirely different nature than the preceding one consisted in this that the hydrogen circulation and the helium circulation could not be worked simultaneously with the available helpers to work them. It is true that the two circulations have been arranged not only for continuous use, but if there is a sufficient number of helpers, also for simultaneous use, but in a first experiment it was out of the question to look, besides after the helium circulation, also after the hydrogen circulation, the working of which requires of course, great experience²⁾. So on the same day that the helium experiment was to be made, a store of hydrogen had to be previously prepared large enough to provide for the required cooling during the course of the helium experiment. It was again the law of corresponding states which directed us in the estimation of the duration of the experiment and the required quantity of liquid hydrogen³⁾. They remained just below the limit at which the arrangement of

¹⁾ [That success was only possible by applying the cycle method is evident from the fact that the helium has passed the valve 20 times before liquefaction was observed, and the considerable labour expended on the preparation of the pure helium would have been increased in the same proportion i.e. to an extravagant amount].

²⁾ [Now the great difficulties of a first liquefaction have been overcome simultaneous working has become possible, though it remains the question how to find the means to develop the laboratory service according to the extension of its field of research].

³⁾ [The hydrogen cycle is not only arranged so that the same pure hydrogen in it can be circulated and liquefied at the rate of 4 liters per hour as long as this is wished, but also allows (as will be treated in a following communication) easily to prepare great stores of extremely pure hydrogen gas, which can be tapped off from the apparatus as liquid at the rate of 4 liters per hour].

the experiment in the designed way would be unadvisable, but how near this limit was has appeared later.

In all these considerations the question remained whether everything that could appear during the experiment, had been sufficiently taken into account in the preparation. So we were very glad when the calculation of the last determined points on the isotherm of -259° shortly before the experiment confirmed that the *BOYLE-point* [though below the boiling point of hydrogen] lay somewhat above this lowest temperature of preliminary cooling, and at least the foundation of the experiment was correct.

In the execution I have availed myself of different means which DEWAR has taught us to use. I have set forth the great importance of his work in the region of low temperatures in general elsewhere (Comm. Suppl. N^o. 9, Febr. 1904), here, however, I gladly avail myself of the opportunity of pointing out that his ingenious discoveries, the use of silvered vacuum glasses, the liquefaction of hydrogen, the absorption of gases in charcoal at low temperatures, together with the theory of VAN DER WAALS, have had an important share in the liquefaction of helium.

§ 2. *Description of the apparatus.* The whole of the arrangement has been represented on Pl. I. We mentioned before that in virtue of the principles set forth in Comm. N^o. 23 the construction of the helium liquefactor (see Pl. II and III) was as much as possible an imitation of the model of the hydrogen liquefactor described before (Comm. N^o. 94^f, May 1906), to which I therefore refer in the first place.

It was particularly difficult to keep the hydrogen, which evaporating under a pressure of 6 cm. is to cool the compressed helium to 15° K. (just above the melting point of hydrogen), on the right level in the refrigerator intended for this purpose. This difficulty was surmounted in the following way. The liquid hydrogen is not immediately conveyed from the store bottles into the refrigerator, but first into a graduated glass *Ga* in the way indicated before, which on comparison of the figures from Comm. N^o. 94^f and N^o. 103 Pl. I fig. 4 does not require a further explanation. This graduated glass was a non-silvered vacuum glass, standing in a silvered vacuum glass *Gb* with liquid air, in which on either side the silver coating had been removed over a vertical strip so as to enable us to watch the level of the hydrogen in the graduated glass. From this vacuum glass the liquid hydrogen is siphoned over into the hydrogen refrigerator by means of a regulating cock *P*. To see whether the level of the liquid in the refrigerator takes up the right position, the german silver reservoir *N₁* of a helium thermometer has been

soldered to the tube which conveys at an initial temperature of -190° the compressed helium which is to be cooled down further. This reservoir leads through a steel capillary N_2 (as in Comm. N^o. 27, May, 1896) to a reservoir N_4 with stem N_3 . The quantity of helium and the pressure have been regulated in such a way that the mercury stands in the top of the stem, when the thermometer reservoir is quite immersed in hydrogen of 15° K, while as soon as the level falls, this is immediately shown by the fall of the mercury. The same purpose is further served by two thermoelements constantan iron (see Comm. N^o. 89 Nov. 1903 and N^o. 95a June 1906) one on the bottom, the other soldered to the spiral on the same level as the thermometer reservoir. They did not indicate the level in the experiment of July 10th, because something got defect.

The evaporated hydrogen contributes in the regenerator Db to save liquid air during the cooling of the compressed helium, and is sucked up (along 15 and Hc) in the large cylindre of the conjugated methylchloride pump (Comm. N^o. 14 Dec. 1894), which otherwise serves in the methylchloride circulation of the cascade for liquid air; it is further conducted through an oil-trap, and over charcoal to the hydrogen gas-holder (Comm. N^o. 94f), from which the hydrogen compressor (Comm. N^o. 94f) forces the gas again into the store cylindres.

To fill the helium circulation the pure helium passes from the cylindres R_1 (see Pl. II), in which it is kept, into the gasholder floating on oil (cf. Comm. N^o. 94f), which is in connection with the space in which the helium expands when issuing from the cock, a german silver cylindre, in which the upper part of the vacuum glass Ea has been inserted. The gas from the gasholder, and afterwards the cold outflowing helium, which has flowed round the regenerator coil, and of whose low temperature we have availed ourselves in the regenerator Da to save liquid air when cooling the compressed helium, is sucked up by the auxiliary compressor V , and then received in the compressor with mercury piston Q (Comp. Comm. N^o. 54). This forces it (Pl. II and III) along the conduit:

a. through a tube Ca which at its lower end is cooled down far below the freezing point by means of vapour of liquid air, and at its upper end is kept at the ordinary temperature. Here the helium is perfectly dried.

b. through a tube divided into two parts along two refrigerating tubes (in Da and Db), in which it is cooled in the one by the abducted hydrogen, in the other by the abducted helium, after which it unites again.

c. through a tube Cb filled with exhausted charcoal immersed

in liquid air. Here whatever traces of air might have been absorbed during the circulation, remain behind.

d. through a refrigerating tube B_2 lying in the liquid air, which keeps the cover of the hydrogen space and of the helium space cooled down.

e. through a refrigerating tube B_2 , in which it is cooled by the evaporated liquid hydrogen.

f. through the refrigerating tube B_1 lying in the liquid hydrogen evaporating under a pressure of 6 cm., here the compressed helium is cooled down to 15° K;

g. and from here in the regenerator coil A , which has been fourfold wound as in HAMPSON's apparatus for air, and in the hydrogen liquefactor of Comm. 94*f*.

Then it expands through the cock M_1 , if it should allow too much gas to pass, this can escape through a safety tube. When the temperature has descended so low that the liquid helium flows out, the latter collects in the lower part of the vacuum glass Ea , which is transparent up to the level of the cock, and is silvered above it.

The outflowing gaseous helium can be made to circulate again by the compressor of the circulation, or be pressed in the supply cylinders R_2 .

At some distance under the expansion cock M_1 , the german silver reservoir Th_1 of a helium thermometer has been adjusted, it is soldered to a steel capillary Th_2 , which is connected with the manometer reservoir Th_4 with stem Th_3 . If the mercury has been adjusted in such a way that at 15° K its level is at the lower end of the just mentioned stem, the stem has sufficient length to prevent the mercury from overflowing into the capillary with further fall of the temperature.

The circulation is provided with numerous arrangements for different operations (for the compressor comp. Comm. n°. 54). Worth mentioning is an auxiliary tube Z filled with exhausted charcoal, which is cooled by liquid air when used. After the whole apparatus has been filled with pure gas, the gas is circulated through this side-conduit (along 11 and 8) while the tube Cb of charcoal belonging to the liquefactor, is shut off (by M and 9), to free it from the last traces of air which might have remained in the compressor and the conduits.

It now remains to describe in what way it has been arranged that the liquid helium can be observed. Round the transparent bottom part of the vacuum glass a protection of liquid hydrogen has been applied. The second vacuum glass E_b , which serves this purpose, forms a closed space together with the former E_a , and the construction

has been arranged in such a way that first this space can be exhausted and filled with pure hydrogen gas, which is necessary to keep the liquid hydrogen perfectly clear later on. The liquid hydrogen is again conducted into this space in the way of Comm. N°. 94^f and 103 Pl. I fig. 4; the evaporated hydrogen escapes at *Hg* to the hydrogen gasholder. The hydrogen glass is surrounded by a vacuum glass *E_c* with liquid air, which in its turn is surrounded by a glass *E_d* with alcohol, heated by circulation.

By these contrivances and the extreme purity of the helium we succeeded in keeping the apparatus perfectly transparent to the end of the experiment, after 5 hours. Protection with liquid hydrogen is necessary to reduce the evaporation of the helium to an insignificant degree notwithstanding that the silver coatings of the vacuum glass have been removed. That it ended in a narrower part, and the helium thermometer reservoir not was placed at the lowest point, was because it was possible that only an exceedingly slight amount of liquid was formed. The vacuum glass was made transparent up to the cock in order to enable us to see any mist that might appear and if on the other hand much liquid was formed, to prevent the lower part from getting entirely filled without our noticing it. The latter has actually been the case for some time, and would not have been so soon perceived, if the walls had been silvered further. But if the glass is not silvered, the conduction of heat towards the helium is much greater, and without protection with liquid hydrogen the helium that was formed, might have immediately evaporated.

In the preparation of the vacuumglasses ¹⁾ Mr. O. KESSELRING, glass-blower of the laboratory, has met the high demands put to him, with untired zeal and devotion, for which I here gladly express my thanks to him.

§ 3 *The helium.* As to the chemical part of the preparation of this gas I was successively assisted by Mr. J. WATERMAN, Mr. J. G. JURLING, Mr. W. MEYER-CLUWEN and Mr. H. FILIPPO Jzn. Chem. Docts., who collaborated with Mr. G. J. FLIM, chief of the technical department of the cryogenic laboratory. To all of them I gladly express my indebtedness for the share each of them has had in the arrangement, the improvement, and the simplification of the operation. More particularly to Mr. FILIPPO for his careful analyses and the effective way, in which the last combustion over CuO with addition of oxygen, and avoidance of renewed contamination by hydrogen was carried out by him.

¹⁾ [There was one of each in reserve before the beginning of the experiment. Only one of the reserves had to be used].

The gas was obtained from the monazite (see § 1) by means of heating, it was exploded with oxygen, cooled with liquid air, and, compressed, led over charcoal at the temperature of liquid air. Then it was burned over CuO. Then it was compressed over charcoal at the temperature of liquid air, after which it was under pressure led over charcoal at the temperature of liquid hydrogen several times till the gas which had been absorbed in the charcoal and then separately collected no longer contained any appreciable admixtures.

This way of preparation (to be treated in a following Comm.) was also applied in Comm. N^o. 105.

§ 4. *The experiment.* After on July 9th the available quantity of liquid air had been increased ¹⁾ to 75 liters, all apparatus examined as to their closures, exhausted, and filled with pure gas, we began the preparation of liquid hydrogen on the 10th of July, 5.45 a.m., 20 liters of which was ready for use in silvered vacuum glasses (cf. Comm. N^o. 94 f Pl. III) at 1.30 p.m. In the meantime the helium apparatus had been exhausted while the tube with charcoal belonging to it was heated, and this tube being shut off, the gas contained in the rest of the helium circulation was freed from the last vestiges of air by conduction over charcoal in liquid air through the side-conduit. The hydrogen circulation of the helium apparatus was connected with the hydrogen gasholder and the air-pump, which had served as methyl chloride pump in the preparation of air the day before, and this whole circulation was exhausted for so far as this had not yet been done, and filled with pure hydrogen. Moreover the space between the vacuum glasses (E_a and E_b) which was to be filled with liquid hydrogen as a protection against access of heat, was exhausted and filled with pure hydrogen, and the thermometers and thermoelements were adjusted.

At 1.30 p.m. the cooling and filling of the glasses which, filled with liquid air, were to protect the glasses which were to be filled with liquid hydrogen, began with such precautions that everything remained clear when they were put in their places. At 2.30 a commencement was made with the cooling of the graduated vacuum glass and of the hydrogen refrigerator of the helium liquefactor by the aid of hydrogen led through a refrigerating tube, which was immersed in liquid air. At 3 o'clock the temperature of the refrigerator had fallen to -180° according to one of the thermo-elements. Then the protecting glass (E_b) was filled with liquid hydrogen, and after

¹⁾ [With the help of the regenerative cascade Comp. Comm. N^o. 94, f. XIII and Supplem. N^o. 18].

some delay in consequence of insignificant disturbances, the filling of the graduated vacuum glass and the hydrogen refrigerator with hydrogen began at 4.20 p.m.

At the same time the helium was conducted in circulation through the liquefactor. The pressure under which the hydrogen evaporated, was gradually decreased to 6 c.m., at which it remained from 5.20 p.m. The level in the refrigerator was continually regulated according to the indication of the thermometer-level-indicator and the reading of the graduated glass, and care was taken to add liquid hydrogen (*Hydr. a, Hydr. b* Pl. II) and liquid air wherever necessary (*a, b, c, d*, Pl. II). In the meantime the pressure of the helium in the coil was slowly increased, and gradually raised from 80 to 100 atms. between 5.35 and 6.35 p.m.

At first the fall of the helium thermometer which indicated the temperature under the expansion cock, was so insignificant, that we feared that it had got defect, which would have been a double disappointment because just before also in the gold-silver thermo-element, which served to indicate the same temperature, some irregularity had occurred. After a long time, however, the at first insignificant fall began to be appreciable, and then to accelerate. Not before at 6.35 an accelerated expansion was applied, on which the pressure in the coil decreased from 95 to 40 atms., the temperature of the thermometer fell below that of the hydrogen. In successive accelerated expansions, especially when the pressure was not too high, a distinct fluctuation of the temperature towards lower values was clearly observed. Thus the thermometer indicated e.g. once roughly 6° K.

In the meantime the last bottle of the store of liquid hydrogen was connected with the apparatus: and still nothing had as yet been observed but some slight waving distortions of images near the cock. The thermometer indicated first even an increase of temperature with accelerated expansion from 100 atms., which was an indication for us to lower the circulation pressure to 75 atms. Nothing was observed in the helium space then either, but the thermometer began to be remarkably constant from this moment with an indication of less than 5° K. When once more accelerated expansion from 100 atms. was tried, the temperature first rose, and returned then to the same constant point.

It was, as prof. SCHREINEMAKERS, who was present at this part of the experiment, observed, as if the thermometer was placed in a liquid. This proved really to be the case. In the construction of the apparatus (see § 2) it had been foreseen that it might fill with

liquid, without our observing the increase of the liquid. And the first time the appearance of the liquid had really escaped our observation. Perhaps the observation of the liquid surface, which is difficult for the first time under any circumstance, had become the more difficult as it had hidden at the thermometer reservoir. However this may be, later on we clearly saw the liquid level get hollow by the blowing of the gas from the valve and rise in consequence of influx of liquid on applying accelerated expansion, which even continued when the pressure descended to 8 atms. So there was no doubt left that the critical pressure lies also above one atmosphere. If it had been below it, the apparatus might all at once have been entirely filled with liquid compressed above the critical pressure, and only with decrease of pressure a meniscus would have appeared somewhere in the liquid layer; this has not taken place now.

The surface of the liquid was soon made clearly visible by reflection of light from below, and that unmistakably because it was clearly pierced by the two wires of the thermoelement.

This was at 7.30 p.m. When the surface had once been seen, it was no more lost sight of. It stood out sharply defined like the edge of a knife against the glass wall. Prof. KUENEN, who arrived at this moment, was at once struck with the fact that the liquid looked as if it was almost at its critical temperature. The peculiar appearance of the helium may really be best compared with that of a meniscus of carbonic acid e.g. in a Cagniard de la Tour-tube. Here, however, the tube was 5 cm. wide. The three liquid levels in the vacuum glasses being visible at the same time, they could easily be compared; the difference of the hydrogen and the helium was very striking.

When the surface of the liquid had fallen so far that 60 cm³. of liquid helium still remained — so considerably more had been drawn off — the gas in the gasholder was exhausted, and then the gas which was formed from this quantity of liquid was again separately collected. In the course of the experiment the purity of this gas was determined by means of a determination of the density (2,01), which was afterwards confirmed by an explosion experiment with oxyhydrogen gas added, and further by a careful spectroscopical investigation.

At 8.30 the liquid was evaporated to about 10 cm³., after which we investigated whether the helium became solid when it evaporated under decreased pressure. This was not the case, not even when the pressure was decreased to 2,3 cm. A sufficient connection could not be

quickly enough established with the large vacuum pump, which exhausts to 2 mm., so this will have to be investigated on another occasion. The deficient connection, however, has certainly made the pressure decrease below 1 cm., and perhaps even lower. That 7 mm. has been reached, is not unlikely.

At 9.40 only a few cm³. of liquid helium were left. Then the work was stopped. Not only had the apparatus been taxed to the uttermost during this experiment and its preparation, but the utmost had also been demanded from my assistants.

But for their perseverance and their ardent devotion every item of the program would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful.

In particular I wish to express my great indebtedness to Mr. G. J. FLIM, who not only assisted me as chief of the technical department of the cryogenic laboratory in leading the operations, but has also superintended the construction of the apparatus according to my direction, and rendered me the most intelligent help in both respects.

§ 5. *Control experiments.* All the gas that had been used in the experiment, was collected in three separate quantities and compressed in cylinders. Quantity *A* contains what was finally left in the apparatus. Quantity *B* has been formed by evaporation of a certain quantity of liquid helium. Quantity *C* is the remaining part that has been in circulation. Together they yielded the same quantity as we started with. They were all three exploded with addition of oxyhydrogen gas and excess of oxygen; no hydrogen could be demonstrated. For the density (in a single determination) we found ($0 = 16$) $A = 2.04$, $B = 1.99$, $C = 2.02$

The spectrum of the gas used for the experiment put in a tube with mercury closure without electrodes and freed beforehand from vapour of water and fat at the temperature of liquid air, answered (only the spectrum of the capillary has been investigated) the description given by COLLIE of the spectrum of helium with a trace of hydrogen and mercury vapour.

Spectroscopically both the distilled *C*, and *B* were somewhat purer than the original gas. In the latter the hydrogen lines gained in case of high vacua, in the former the helium disappeared last. The hydrogen, from which the latter has still been cleared, must be found in *A*. By means of absorption by charcoal 8 c.m³. of hydrogen was separated from this. To this would correspond a difference in percentage of hydrogen before and after the experiment of 0.004 %.

To estimate the percentages of hydrogen the spectra of the just-mentioned quantities were compared with the spectrum of a helium which could not contain much more than 0.005 % hydrogen according to an estimation founded on the quantities of hydrogen which had been absorbed from the gas the last few times of successive purification when it was led compressed over charcoal at the temperature of liquid hydrogen, and with the spectrum of this helium after 0,1 % hydrogen had been mixed with it.

The gas used for the experiment did not differ much from that which served for comparison, and of which the red hydrogen and the helium lines vanished simultaneously for the highest vacua, but it seemed to be somewhat less pure, for the red hydrogen line preponderated over the helium line for the highest vacua. In the different spectra the hydrogen line was not to be seen at a pressure of 32 mm., the *H*-line with an intensity of 0,01 of He 5016; at 12—16 mm. *C* was faint compared with He 6677, and *F* faint compared with He 5016. An amount varying between 0,01 and 0,3 was assumed for the ratio of the intensity.

On the other hand at 32 mm. the *C* in the mixture with 0,1 pCt. hydrogen had already the same intensity as He 6677, *F* 0,3 of He 5016, which remained the case at 16 mm. (somewhat less for *C*, somewhat more for *F*).

In spite of the precautions taken it was observed a single time that the hydrogen lines increased in intensity during the determination, so when we proceeded to lower pressures the determinations became unreliable. These comparisons are, therefore, very imperfect; but then, the examination how traces of hydrogen in helium may be quantitatively determined by a spectroscopic method would constitute a separate investigation. In connection with the above difference in content of *B* and *C* with the original gas, the observations mentioned may perhaps serve to show that these percentages have not been much more than 0,004 and 0,008.

The purity of the helium had already been beyond doubt before, for the cock worked without the least disturbance, and no turbidity was observed even in the last remaining 2 cm³. of liquid.

The reliability of the helium thermometer was tested by the determination of the boiling point of oxygen, for which 89° K. was found instead of 90° K. We must however, bear in mind that the thermometer has not been arranged for this temperature and the accuracy in percents of the total value is considerably higher for the much lower temperature of liquid helium.

For the assistance rendered me in the different control experiments, I gladly express my thanks to Dr. W. H. KEESOM and Mr. H. FILIPPO Jzn.

§ 6. *Properties of the helium.* By the side of important points of difference the properties of helium present striking points of resemblance with the image which DEWAR drew in his presidential address in 1902 on the strength of different suppositions.

We mentioned already the exceedingly slight capillarity.

For the boiling-point we found $4^{\circ}.3$ on the helium thermometer of constant volume at 1 atm. pressure at about 20°K . This temperature is still to be corrected to the absolute scale by the aid of the equation of state of helium. The correction may amount to some tenths of degrees if a increases at lower temperatures, so that the boiling-point may perhaps be rounded off to $4^{\circ}.5\text{ K}$.

The triple-point pressure if it exists lies undoubtedly below 1 cm., perhaps also below 7 mm. According to the law of corresponding states the temperature can be estimated at about 3°K at this pressure. The viscosity of the liquid is still very slight at this temperature. If the helium should behave like pentane, we could descend to below 1.5°K before it became viscous, and still lower near 1°K before it became solid. How large the region of low temperatures (and high vacua) is that has now been opened, is, however, still to be investigated.

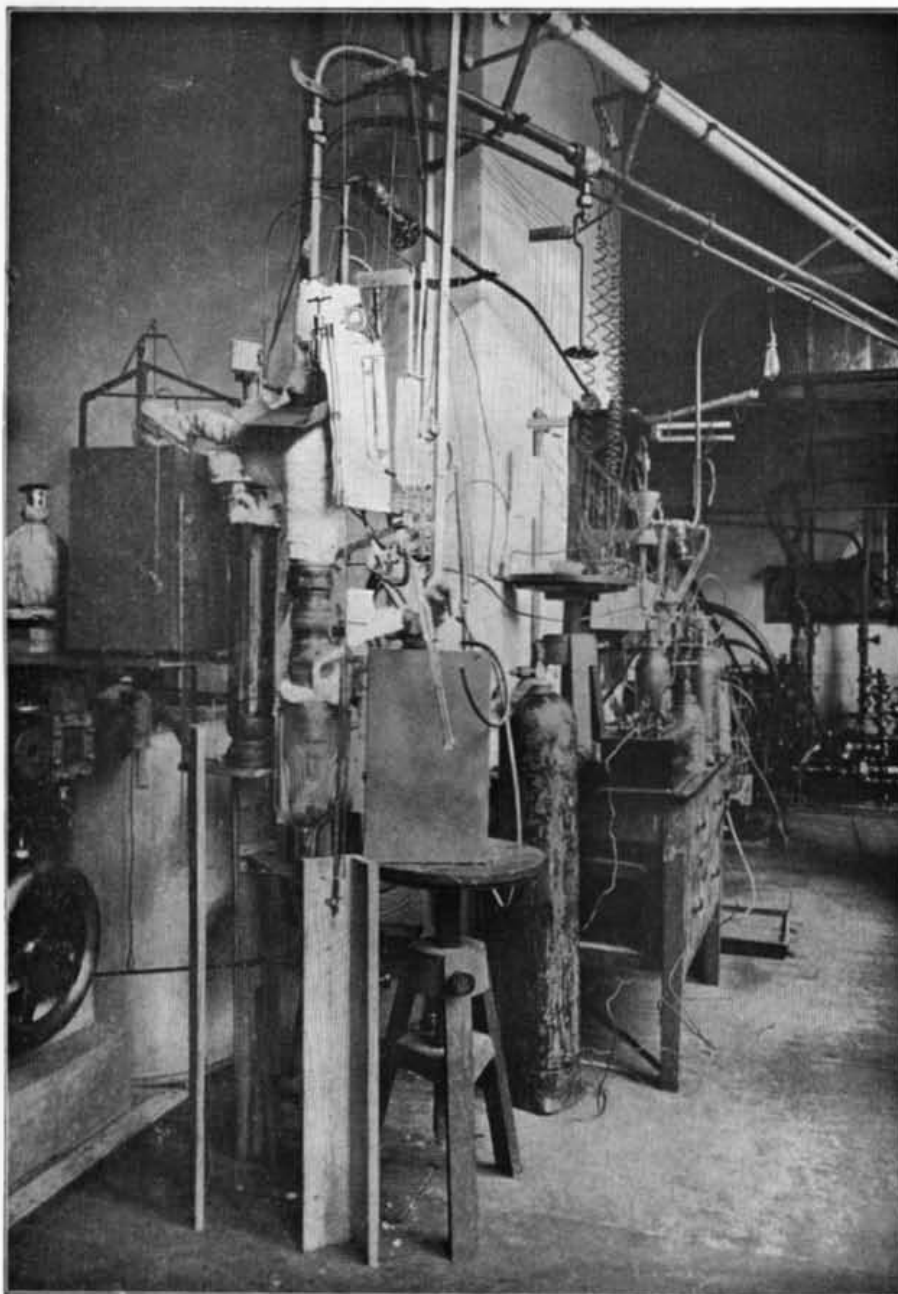
Liquid helium has a very slight density, viz. 0.15. This is smaller than was assumed and gives also a considerably higher value of b than can be derived from the isotherms at $-252^{\circ}.72$ and $-253^{\circ}.82$ now that the points mentioned in § 1 have been determined, viz. about 0.0007 provisionally. The value of b which follows from the liquid state is about double the value of b which was expected [viz. 0.0005], and was assumed in the calculations of Dr. KEESOM and myself on mixtures of helium and hydrogen (Comp. Suppl. N^o. 16 Sept. '07 § 1 fn. 5).

From the high value of b follows immediately a small value of the critical pressure, which probably lies in the neighbourhood of 2 or 3 atms., and is exceedingly low in comparison with that for other substances. So when helium is subjected to the highest pressures possible, the "reduced" pressures become much higher than are to be realized for any other substance. What may be obtained in this respect, by exerting a pressure of 5000 atms. on helium exceeds what would be reached when we could subject carbonic acid e.g. to a pressure of more than 100.000 atms.

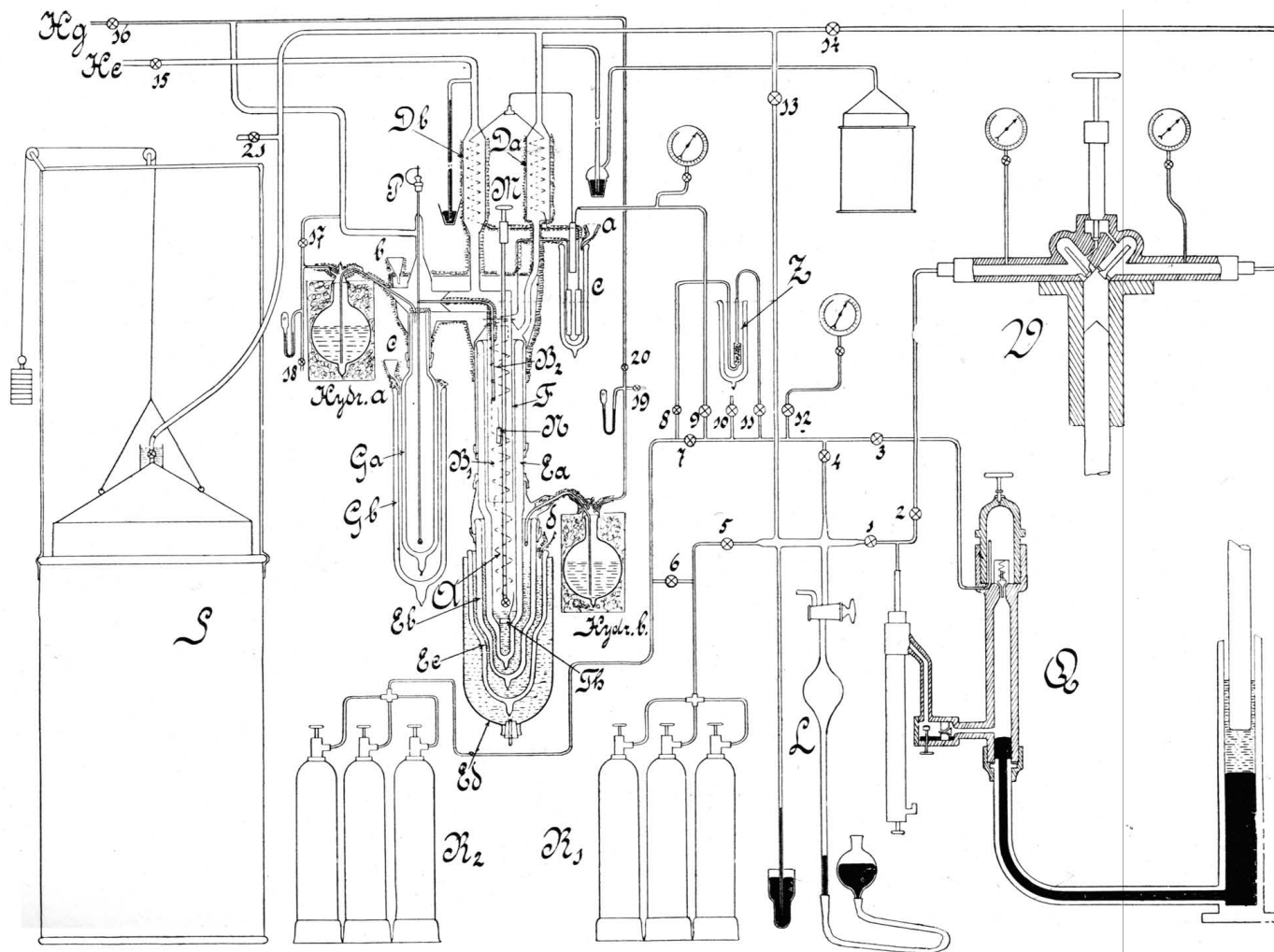
The ratio of the density of the vapour and that of the liquid is

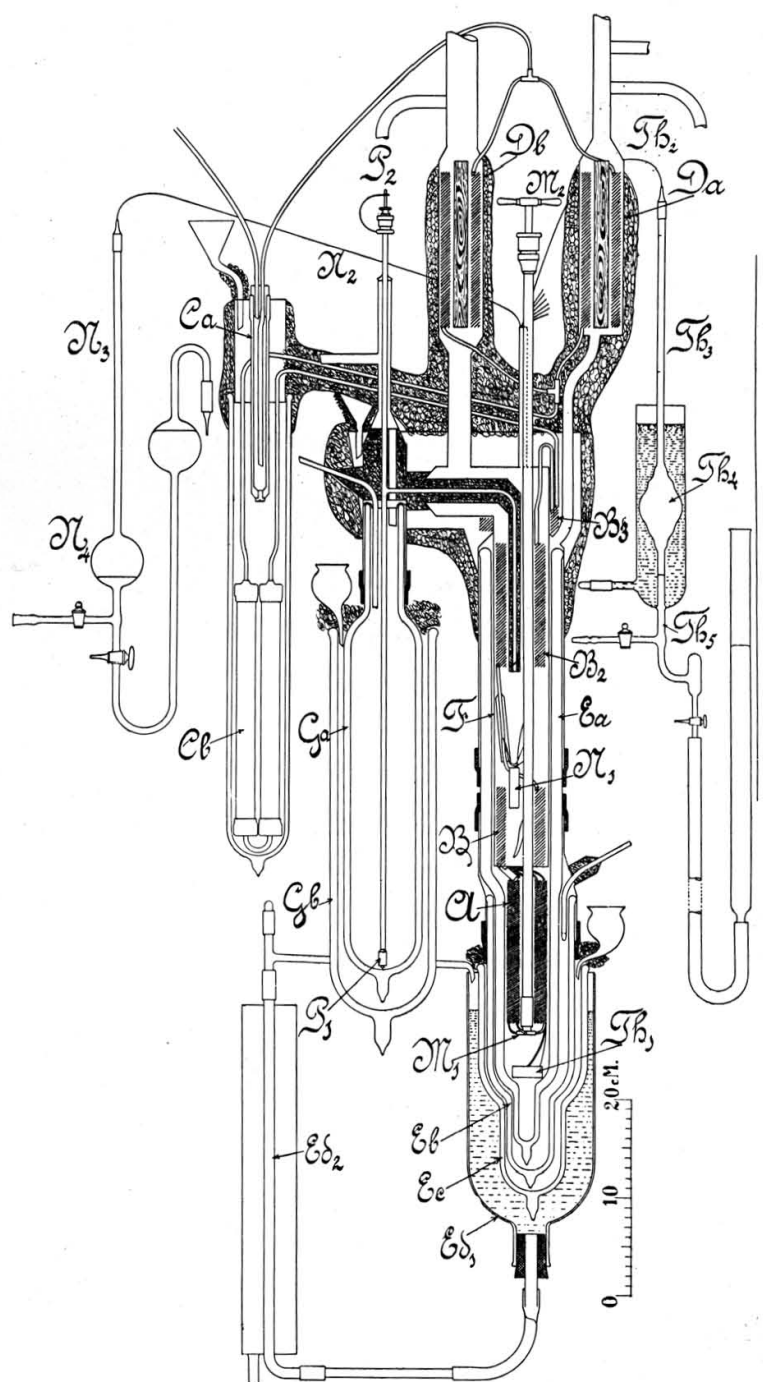
H. KAMERLINGH ONNES. "The liquefaction of helium."

Plate I.



Proceedings Royal Acad. Amsterdam. Vol. XI.





about 1 to 11 at the boiling-point. It points to a critical temperature which is not much higher than 5° K., and a critical pressure which is not much higher than 2,3 atms.

But all the quantities mentioned will have to be subjected to further measurements and calculations before they will be firmly established, and before definite conclusions may be drawn from them.

We may only still mention here a preliminary value of a , viz. 0.00005. When in 1873 VAN DER WAALS in his Dissertation considered whether hydrogen would have an a , it was only after a long deliberation that he arrived at the conclusion that this must exist, even though it should be very small. It may be presumed that matter will always have attraction, was his argument, and as chance would have it these words were repeated by him in reference to helium some days before the liquefaction of helium (These Proc. June 1908). The a found now denotes the smallest degree of this attraction of matter, which still manifests itself with remarkable clearness also in helium in its liquefaction.

Geology. — *"The age of the layers of Sondé and Trinil on Java"*.

By Prof. K. MARTIN.

(This paper will not be published in this Proceedings).

(September 8, 1908).