

Physics. — “*Solid helium*”¹⁾. By W. H. KEESOM. (Communication N^o. 184*b* from the Physical Laboratory at Leyden).

(Communicated at the meeting of September 25, 1926).

§ 1. *Introduction.*

On the same day that KAMERLINGH ONNES liquefied helium for the first time, he investigated whether it would become solid on further cooling by evaporation under reduced pressure. He was at that time able to obtain a vapour pressure below 1 cm, probably 7 mm²⁾. The helium however remained liquid.

This attempt to solidify helium by reducing the pressure under which it evaporates, was repeated on several occasions. In 1909 KAMERLINGH ONNES was able to reduce the pressure to 2.2 mm (the temperature then was estimated at 2.5 to 2° K., now put at 1.4° K.)³⁾; in 1910 a pressure of even 0.2 mm was reached (temperature 1.15° K.)⁴⁾. But the helium still remained a thin liquid.

The further development of the question, whether helium could be made to freeze on still further cooling, was then postponed in favour of more urgent questions, which could be dealt with the means available, while for the investigation of the solidification of helium new means were necessary.⁵⁾

A new attempt was made in 1919, but with little improvement. Then in 1921 KAMERLINGH ONNES⁶⁾ by making use of a battery of condensation pumps, reached a remarkably lower pressure, probably 0.013 mm, at any rate less than 1/50 mm, at which, after estimation, the temperature should be 0.82° K.

Meanwhile helium still remained liquid, so that KAMERLINGH ONNES wondered whether helium would perhaps remain liquid even if it were cooled to the absolute zero. In order to obtain further data about this question KAMERLINGH ONNES still before his retirement procured a much more powerful mechanical pump installation, and further, a condensation pump of greater power was constructed with which we intend to reduce the temperature again.

¹⁾ Provisional communications were published in C. R. **183**, 26 and 189, July 5 and 19, 1926, and Nature July 17, 1926.

²⁾ These Proc. **11**, 168, 1908; Comm. Leyden, N^o. 108.

³⁾ These Proc. **12**, 175, 1909; Comm. Leyden, N^o. 112.

⁴⁾ Jubilee-Book VAN BEMMELEN 1910. See also Comm. Leyden N^o. 119, p. 12 and Comm. Leyden Suppl. N^o. 35, p. 29.

⁵⁾ See KAMERLINGH ONNES, Comm. Leyden N^o. 159, § 4.

⁶⁾ H. KAMERLINGH ONNES, Comm. Leyden N^o. 159.

Meanwhile the results of the provisional experiments of KAMERLINGH ONNES and VAN GULIK¹⁾ about the change of the melting point of hydrogen by pressure, had made me wonder, if it would not be possible at the temperatures already reached, to solidify helium by pressure. This idea became still more definite on considering the results of the measurements of SIZOO and KAMERLINGH ONNES²⁾ about the influence of allsided compression on the supraconductivity: so fig. 5 of Comm. N^o. 180*b* raised the question, whether the small difference between the lines for 193 and for 300 KG/cm² (according to the authors hardly more than experimental error), would not be explained thus: that the helium had become solid in the compression tube and that because of the adhesion to the wall an increase of the pressure put on had not caused a corresponding increase of the pressure upon the investigated thread³⁾.

§ 2. *Solidification of helium* (June 25th 1926). *Provisional determination of the melting curve.*

a. *Method.* The criterion for judging if helium had become solid, and

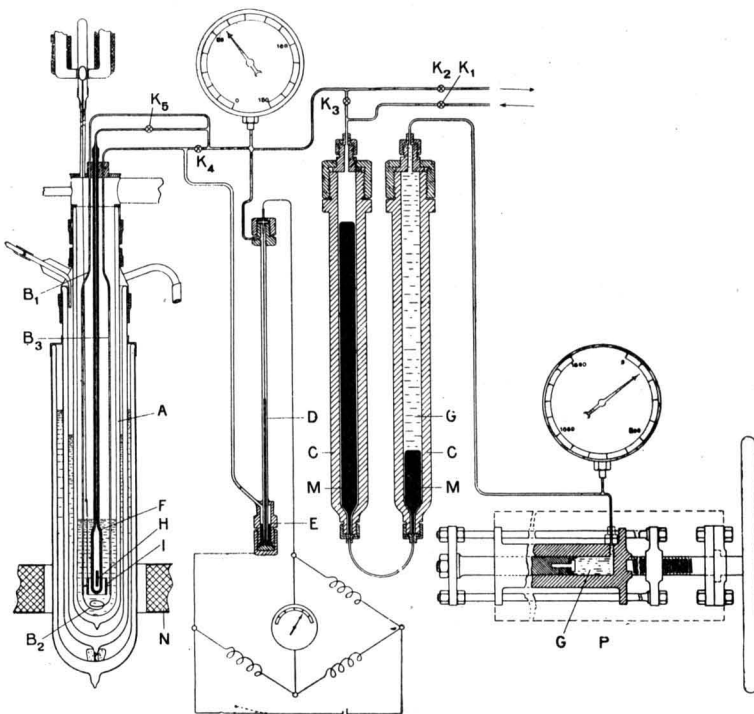


Fig. 1.

1) H. KAMERLINGH ONNES and W. VAN GULIK, These Proc. 29, p. 1184, 1926; Comm. Leyden N^o. 184a.

2) These Proc. 28, 656, 1925; Comm. Leyden N^o. 180*b*.

3) See also G. J. SIZOO, W. J. DE HAAS and H. KAMERLINGH ONNES, Comm. Leyden N^o. 180*c*, p. 32 and fig. 2.

the method for determining the melting curve of the solid helium were the same as those followed by KAMERLINGH ONNES and VAN GULIK (l.c.) in determining the melting curve of hydrogen.

In fig. 1, B_1 and B_3 are two tubes of new silver, which are connected at the bottom, in the cryostat vessel A , by a narrower brass tube B_2 . Here the helium is compressed. Therefore firstly the wheel of the hydraulic pump P , which is filled with glycerine G , is turned back. CC are two vessels, connected by a tube, which are half-filled with mercury M . By turning back the wheel, glycerine comes into the pump, the mercury rises in the right hand vessel C , and falls in the left hand one. So the left hand vessel gets filled with helium gas, which is supplied by the stop-cock K_1 (K_3 is shut). Then K_1 is shut, K_3 opened. K_4 is open, K_2 shut¹⁾. Now by turning the wheel of the hydraulic pump to the right the helium gas is compressed into the tubes B , in which it liquefies, and collects in the lower part of the tube. At a pressure of 400 KG/cm² all connections were still tight.

In order to determine if helium had solidified, the following apparatus was used, constructed by G. J. FLIM, chief of the technical staff of the cryogenic laboratory. D works as a differential manometer, and consists of a steel tube, which runs into the mercury-chamber E . When K_2 is opened slightly, K_4 and K_3 being shut, and the tube B is blocked by a piece of solid helium, so that a pressure difference appears between B_1 and B_3 , the pressure in D becomes less than the pressure in E , and the mercury in D rises. Along the axis of D a thin platinum wire was stretched, which formed one of the branches of a Wheatstone bridge. Now when mercury rises in D the resistance of this branch decreases, and the needle of the galvanometer becomes deflected.

b. The experiments. In the first experiment the pressure of the helium bath was lowered as much as possible by the means ordinarily at hand in the laboratory (Burckhardtpump, 360 m³/hour), namely to approximately half a millimeter mercury pressure. Within the capillary B the pressure was put at 250 KG/cm²²⁾. In the Wheatstone bridge the galvanometer was at equilibrium. When the stopcock K_2 was opened slightly, the galvanometer needle showed a deflection. This indicated that the capillary B was blocked.

The temperature of the bath was now raised till the pressure was 1 atm. The capillary remained blocked.

The pressure in the capillary was lowered. At 150 KG/cm² the capillary was still blocked. At 100KG/cm² blocking had disappeared. At

¹⁾ In the experiments of June 25th the side-tube with stopcock K_5 and the glass piezo-meter F were not present, in the experiments of July 1st K_5 was shut during the operation described above.

²⁾ Here are given the apparent readings of the metalmanometer. In table I the corrections are applied.

130 KG/cm² the capillary was blocked again, as also at 128. At 125 KG/cm² it was open, and at 126 KG/cm² also.

Inference: at 126 KG/cm² helium is liquid, at 128 KG/cm² it is solid.

As in this experiment there was no stirrer in the cryostat, the temperature of the bath under the liquid surface was uncertain ¹⁾.

The pressure of the helium bath was then reduced to about ²⁾ 400 mm. At 120 KG/cm² the capillary was blocked; so it was at 115.

At 110 KG/cm² capillary opens.

„ 112 „ „ blocked.

„ 111 „ „ still blocked.

„ 110 „ „ opens.

This result clearly showed that we were on the track of the melting curve of helium.

The pressure of the helium bath was reduced to about 200 mm.

At 95, 92, 90, 88 KG/cm² capillary is blocked.

„ 85 „ „ opens.

„ 8 „ „ blocked.

„ 80 „ „ opens.

Reduced to about 100 mm.

At 80, 74, 69, 67 KG/cm² capillary blocked.

„ 63, 65 „ „ open.

„ 70 „ „ blocked.

„ 65 „ „ open.

Reduced to about 50 mm.

At 55, 52 KG/cm² capillary blocked.

„ 50 „ „ blocking disappears gradually.

The bath was then brought to atmospheric pressure, but the observations were irregular; apparently the temperature of the bath was not uniform.

The bath was then reduced to about 400 mm. At 110 KG/cm² the blocking was gradually disappearing. On repetition the same was observed at 109 KG/cm². Thus the same result was obtained as in the first experiment at this temperature (see above). The phenomenon is reproducible.

¹⁾ Indeed it appears from the results, obtained in the repetition of the experiment on July 1st, that the temperature in the lower parts of the bath was below the boiling point of helium.

²⁾ Exact measurements were not made in this first series of experiments.

The provisional results, obtained on this day, are collected in the following table:

TABLE I.

Pressure of the helium bath	Temperature ¹⁾	Melting pressure			Difference with determination of July 1st
		Manometer reading	Corrected ²⁾ KG/cm ²	Atm.	
400 mm	3.61° K.	110	109 ⁵	106	— 2
200	3.12	86	83	81	— 1
100	2.73	65	63 ⁵	61 ⁵	— 1 ⁵
50	2.40	50	48	46	— 1

§ 3. *Repetition on July 1st. Determination of the melting curve. Visual observations.*

a. Determination of the melting curve of helium. Notwithstanding the distinctness of the phenomena I wished to make quite sure and to repeat the experiment. This was done on July 1st.

This time a stirrer (*I* in fig. 1, a hollow soft-iron cylinder, see under *b*, provided with a couple of little paddle-boards in order to stir the liquid) was introduced into the bath, and further arrangements were made, in order to be able to take more exact measurements³⁾. Further it was intended to continue the melting curve to the lowest temperatures, which could be reached with the mechanical vacuum pumps.

Moreover, now that it had appeared that the pressures ought not to be so excessively high, I wished to make the experiment in a glass piezometer, so as to be able to see what happened.

The determination of the melting curve occurred in exactly the same way as the provisional determinations mentioned in § 2*a*. The phenomena took place regularly. The melting pressure, corresponding to a definite temperature, could be fixed to some few tenths of an atmosphere. In some cases the fusion-process could be followed on the pointer of the galvanometer.

For the sake of brevity only the results obtained are given here.

¹⁾ From the pressure of the bath calculated after the formula of Comm. Leyden N^o. 147*b*.

²⁾ The metal manometer used (reaching to 400 KG/cm²) was gauged to 100 KG/cm² with the aid of the closed hydrogen manometers M_{60} and M_{120} . Above this it was compared with the pressure balance of the VAN DER WAALS foundation at Amsterdam. I render therefore my cordial thanks to Dr. A. MICHELS, assistant of this foundation.

³⁾ The pressure of the bath, from which the temperature was derived, was read off by Miss J. L. SOLLEWIJN GELPKKE, phil. nat. cand.; for this aid I render to her my cordial thanks.

TABLE II.

Melting curve of helium		
Pressure of the helium bath	Temperature	Melting pressure
77.09 cm	4.21 °K.	140.5 atm.
40.03	3.61	108.8
20.01	3.12	81.5
9.94	2.72	62.8
5.02	2.40	48.6
2.00	2.04	35.7
1.10	1.83	29.8
0.57	1.60	27.4
0.24	1.42	26.5
0.057	1.19	25.3

The temperatures from 4.21 down to and including 1.60° K. are derived from the pressures of the helium bath according to the formula of Comm. N^o. 147b¹⁾, the two lowest temperatures from the formula which is given by VERSCHAFFELT in Comm. Leyden Suppl. N^o. 49, p. 26²⁾.

The melting pressures were read off on a metal manometer (reading to 150 KG/cm²) which was gauged to 100 KG/cm² with the aid of a manometer, which was itself compared with the closed hydrogen manometers M_{60} and M_{120} ³⁾.

1) H. KAMERLINGH ONNES and S. WEBER. These Proc. 18, 493, 1915.

2) In the provisional communication in the C.R. for these lowest temperatures, values are also communicated which were calculated from a former formula of VERSCHAFFELT (Thesis for the Doctorate TUIYN, Comm. Leyden N^o. 181). I prefer now the values only given here.

3) When the experiments mentioned in § 4 were finished, it was found that the pointer of this manometer was not securely fastened on its axis, and that the zero reading was changed.

As it is not sure if this occurred before or after the experiment of July 1st, these pressure measurements must not be considered absolutely sure. Also for the same reason the corrections above 100 KG/cm² could not be determined afterwards. They were derived from comparison of the manometer with the pressure balance of the VAN DER WAALS foundation, done in Sept., by adopting a constant zero change. This zero change is derived from the difference between this gauging with the pressure balance and the gauging with M_{60} and M_{120} , mentioned in the text, for pressures below 100 KG/cm². I give here the results which for the moment I think to be the most probable ones, reserving the right to repeat this measurement.

[Such a repetition took place at Nov. 26th, 1926. The pressures of table II were confirmed within some tenths of an atmosphere. At the average the readings were 0.6 atm. higher at Nov. 26th. Added in the translation.]

These measurements are sufficiently in agreement with those of § 2a (table I) to form a confirmation of the observations of June 25th.

In fig. 2 the melting curve is represented.

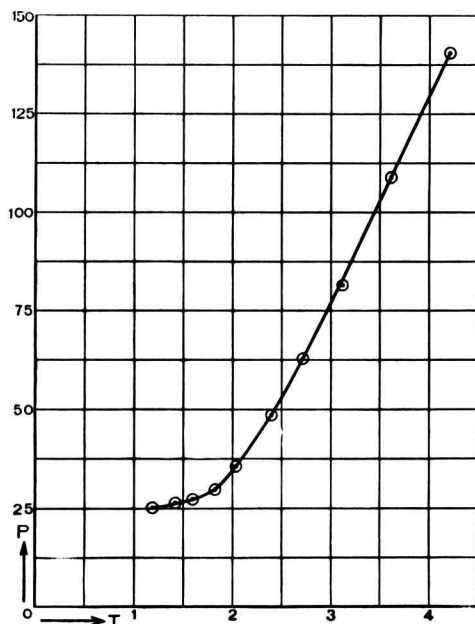


Fig. 2.

The melting curve shows an important peculiarity: it bends at the lowest temperatures so as to become more and more parallel to the T -axis. It shows no tendency at all to meet the vapour pressure curve in a triple-point¹⁾. So unless the melting curve bends down again to the T -axis at still lower temperatures, it will never be possible to solidify helium, liquid under its own saturation pressure, by lowering the temperature alone. So the surmise expressed by KAMERLINGH ONNES (see § 1) that helium (under its own saturation pressure) remains liquid down to the absolute zero (perhaps gradually changing into the vitreous amorphous state), would be established.

In the supposition mentioned, that the melting curve does not bend down again at lower temperatures so that the melting curve and the vapour pressure curve do not meet, as long as we remain below the liquid-gas critical temperature, coëxistence between solid and gas is not possible. Then there is no sublimation curve; evaporation of the solid into the gaseous state will not be possible at those temperatures, the

¹⁾ As Prof. KRUYT pointed out to me, the possibility that this might occur with some substance was already foreseen by H. W. BAKHUIS ROOZEBOOM, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, Braunschweig 1901, p. 93. (Note added in the translation).

solid will always melt first¹⁾. This is yet another peculiarity, which distinguishes helium from all other substances as far as we can judge from observations already made.

The approaching to zero of dp/dT of the melting curve indicates according to the equation of CLAPEYRON, that the heat of fusion approaches in a higher power of T to zero than $T(v_{liq} - v_{sol})$. This is in agreement with the heat theorem of NERNST, when this is applied to the change liquid-solid helium, and perhaps forms, as EHRENFEST remarked, one of the most elementary confirmations of it.

b. Visual observations on the solidification of helium. For this purpose there was brought into the helium cryostat a glass piezometer F (inner diam. 7, outer diam. 13, length 90 mm), into which the helium was supplied by stopcock K_5 . Inside this piezometer was a small soft-iron rod H , which functioned as an electromagnetic stirrer (method of KUENEN). It was moved up and down with the aid of the cylinder I , which was magnetized by the current passing through the windings of the coil N . The cylinder I served also for stirring the helium bath, in order to obtain a uniform temperature (see under a).

After the measurements, mentioned under a, were finished helium was compressed into the glass piezometer.

The pressure of the helium bath was 13.3 mm, to which corresponds a temperature of 1.90° K. While the pressure within the piezometer was increased²⁾, the stirrer was constantly moved up and down. At a certain pressure the stirrer stuck; the helium had become solid. There was however nothing peculiar to be seen in the tube. Solid helium is perfectly transparent.

On decreasing the pressure the stirrer becomes free. Increase of pressure makes the stirrer stick again. These experiments were finished at 3^h.30.

The experiment was repeated at 5^h.30. The level of the helium bath was now somewhat higher (about $\frac{2}{3}$ of the piezometer was in the

¹⁾ When the melting curve continues to temperatures above the liquid-gas critical temperature, of course for those temperatures there will be a direct evaporation of the solid into the gaseous state.

²⁾ There now separated from the helium at the top of the tube a white flaky mass, which stayed for some time in this position, giving the impression of being of very loose structure. By the action of the stirrer H , small pieces occasionally got loose, and sank down in the liquid helium. They probably consisted of condensed oil vapours, which were present in the helium coming from the cycle in more than the usual (very small) quantity, because, during the preceding experiments the helium liquefactor was heated, and the oil vapours which had collected in it in the condensed state, were now scattered throughout the helium gas, particularly in that part of the cycle from which the gas to be compressed was sucked into the piezometer.

In the course of the experiment by the action of the stirrer this mass is spread over the inner wall as a nearly invisible deposit. On repetition of the experiment, in which the piezometer was filled, while the helium liquefactor was still cold, so that the oil vapours remained in the liquefactor, this phenomenon did not occur.

liquid ¹⁾). The pressure of the helium bath was now 200 mm, corresponding to a temperature of 3.12° K.

At 90 KG/cm² the stirrer is still loose, at 90.5 KG/cm² it sticks. On decreasing the pressure to 87 KG/cm² it becomes loose again. Evidently there is some delay in the phenomenon, as a result of the less rapid temperature adjustment owing to the thickness of the glass walls. Otherwise this observation is sufficiently in agreement with that of table II, for complete confirmation, that in these experiments we had observed helium solidifying.

Again there is nothing peculiar to be seen in the helium; no surface of demarcation between solid and liquid, nor between solid and gas or between liquid and gas ²⁾.

There was no indication of difference in refraction, nor change of volume. Evidently the densities and the refractive indices of the different phases under these pressures are nearly equal.

Helium solidifies to a homogeneous transparent mass. That it is a crystalline mass, seems to follow from the fact that the melting curve is sharply defined (comp. under a).

The following detail of the experiment is very instructive. At one moment the helium was liquid in the lowest part of the glass tube, where the stirrer was affixed; above it was a mass of solid helium. This appeared from the fact that the stirrer could be moved only to a definite height, where it collided against the solid block. We were able to hammer the solid helium. Very gradually the stirrer could be moved higher and higher; the block slowly melted down, probably in consequence of the temperature increasing slowly by the radiation of the lamp, which served for illumination.

Even now there was no limiting surface between solid and liquid to be seen.

§ 4. *Demonstration on July 7th.*

I had the pleasure on the occasion of the American week to demonstrate the solid helium to the American students who payed a visit to the laboratory and to some colleagues and others who were interested in it. The experiment of hammering against the block could now be repeated several times. When helium has solidified by increasing the pressure just a little above the melting pressure, and we then decrease the pressure a little, sufficiently to melt the helium slowly, the melting occurs firstly round the stirrer, the stirrer absorbing the radiation of the illumination lamp more than the transparent helium and so acquiring a slightly higher

¹⁾ In the preceding experiment $\frac{1}{4}$, about the length of the stirrer, 23 mm.

²⁾ As regards the last it should be noted, that immediately above the level of the helium in the bath there is a large temperature gradient, so there must be a rapid transition from either the liquid or the solid phase to the gaseous one.

temperature than the helium. So the stirrer gets loose before the helium melts "en masse".

The following observation is very well worth mentioning.

Towards the end of the demonstration, the helium being compressed in the tube more than ten times, there were in the compressed helium some very small dark particles, apparently oxide from the metal tube, which connects the glass experimenting tube with the other apparatus. Then on one occasion I noticed that, resulting from a blow of the stirrer, a mass of helium of about 15 to 20 mm in height was moving as one block over a distance of some millimeters. The small dark pieces made this visible.

In the experiments of this day slight indications of striae near the limit between liquid and solid were seen.

It is an agreeable duty to me to render my cordial thanks to G. J. FLIM, chief of the technical staff, and to L. and A. OUWERKERK, technicians to the cryogenic laboratory, for their intelligent aid.
