Physics. — "Further experiments with liquid helium. BA. Preliminary determinations of the latent heat of vaporization of liquid helium."
By L. I. Dana¹ and H. Kamerlingh Onnes. (Communication No. 179c from the Physical Laboratory at Leiden).²

(Communicated at the meetings of June 27, and December 19, 1925). The object of these experiments was to measure the latent heat of vaporization of liquid helium for pressures at and below one atmosphere by a simple method. Measurements of this thermal constant have not previously been made. They are of especial importance in the problems which present themselves at the lowest temperatures with liquid helium, as a check on the helium temperature scale, and for the purpose of correlation with the vapor pressure and density data by means of the Clausius-Clapeyron equation.

Description of the Method and Apparatus.

It was decided to adopt as simple a method as possible because the operation of the helium cryostat involves a sufficient number of difficulties without introducing extra ones. Fig. 2 shows the calorimeter set up in the helium cryostat, the latter being the same as that described previously in Comm. No. 159 with the exception that in these experiments the helium flask was longer than usual. Fig. 1 shows the calorimeter itself drawn on a larger scale. The latter consists of a small Dewar flask supported by an outlet tube C and containing an electric heating coil P. Through a small valve E the flask could be filled with liquid helium from the surrounding bath. The initial level of the helium was read off by a cathetometer from the millimeter marks engraved on the inner tube. After a current was passed through and the power measured, the final level was ascertained. From the volume and density of the liquid evaporated and the power input, the latent heat could be readily computed.

Before the sealing of the lower part of the calorimeter, the inner tube was carefully calibrated with mercury. Then followed the insertion of the heating coil and the sealing and evacuation of the flask. The heating coil, of 0.1 mm. constantan wire and of 100 ohms resistance, was wound in bifilar fashion on a mica frame. The current leads, of 0.2 mm. copper wire, led out through two side tubes F and F'. Fig. 1, while the openings at the ends of the tube were closed with small brass caps soldered to

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the glass. It was permissible to connect the current leads outside the calorimeter since the resistances of those within were negligible in comparison to that of the heating coil; this procedure dispensed with two extra outlet tubes.

The helium could have been condensed into the calorimeter under pressure, but as it was not allowed to have the level of the helium in the
cryostat above the part protected by the vacuum the time of filling would have been excessive. The use of the small valve $E$ made it possible to fill the calorimeter quickly and thus to make a number of determinations on one day. A copper capillary $D'$ made connection from the valve to the calorimeter, one end being soldered to the bottom of the valve and the other to the inlet tube $D$. To prevent the valve from rotating when the valve stem was turned, and the consequent breaking off of the glass tube $D$, the outer shell of the valve was soldered to the glass tube $H$, which reached to the head of the cryostat, and was there cemented in place. Steel is so hard at low temperatures that a steel valve stem would not make a tight fit with a steel seat; hence the seat was made of brass, while the stem consisted of hardened steel. A long handle, made of german silver tubing to reduce conduction of heat, fitting through a packing gland at the head of the cryostat, actuated the valve stem.

Initially, the diameter of the outlet tube was about 7 or 8 mm. It developed on trial that at the lower pressures of evaporation, below 10 mm. Hg or so, the frictional resistance to the flow of the helium at the rates of evaporation maintained was so great that with the lowest pressures which could easily be maintained with the pump at the top of the outlet, the pressure in the calorimeter was considerably higher. This necessitated a larger outlet tube (see Fig. 2) and, in addition, another concentric tube, leading to the top of the calorimeter, was installed as a static pressure measuring tube; thus no error as a result of a pressure drop could be introduced. The impact pressure of the helium flowing against the central tube was found to be negligible.

Obviously, to fill the calorimeter with helium a sufficient quantity had to be formed to cover the valve; further, it was desirable at all times to have a considerable height of the liquid to cut down heat leaks. It is evident that if the vapor pressure of the liquid inside the calorimeter is somewhat higher than that outside along the outlet tube, or what amounts to the same thing, if the temperature inside is slightly higher, then, while the vapors resulting from evaporation passed through the outlet tube, they would come in contact with the glass wall cooled by the colder liquid and would partly condense, the result being a large value of the observed latent heat. Thus previous to and during evaporation it was essential to keep the vapor pressure of the helium in the outside bath somewhat higher than inside the calorimeter in order that the vapors should be allowed to come in contact only with warmer spots than itself. This pressure difference was maintained by a valve $K$, Fig. 2, connected to the calorimeter and the vacuum line, and observed on a differential oil manometer $G$, one leg of which led from the outer bath and the other to the calorimeter. The differential height of the oil was so regulated as to give at the various pressures of evaporation a temperature difference of $0.05^\circ$ C., — one which experiment showed to
To help maintain uniformity in temperature in the outer bath, a pump stirrer, shown in Fig. 2, was situated by the side of the calorimeter.

To read the levels of the helium meniscus, the lighting of the bath had to be arranged with care. The line of sight was tangent to the millimeter marks. Slits in the silvering of the liquid air and liquid hydrogen flasks, which surrounded the helium flask, limited the light passage; the lower part of the helium flask was unsilvered. Although the rays passed through eight glass walls, the distortion appeared to be small. A low wattage electric lamp behind the outer flask furnished the illumination and an alum cell between the two absorbed the infra-red rays. By inserting a sheet of black paper between the cell and slit, and by raising it till the edge stood just below the meniscus, the latter could be made to stand out sharply. This screen also served to protect most of the liquid in the calorimeter from the lamp rays, with the result that evaporation due to external radiation remained very small.

A Wolff potentiometer of the Diesehorst type served to measure the current by determining the potential drop across a standard in series with the heating coil, and to measure the voltage across the heating coil by ascertaining the potential drop across a part of a standard resistance shunted across the heating coil. Proper corrections were always made for the current shunted through the standard resistance. The time of power input averaged 1000 seconds and to measure it a stop watch was employed.

Heat Leaks and other Sources of Error.

Perhaps the greatest difficulty to overcome in the study of the calorimetric properties of helium is the leakage of heat, because of the low density and the consequent small mass of liquid that can be put into the calorimeter, and principally because of the very low value of the latent heat, which is the smallest of any substance. The enclosure of the liquid to be measured in a small Dewar flask helps greatly in the limiting of the leakage from the surroundings, but the necessity of having current leads and of maintaining a slightly higher temperature in the liquid outside introduces an unavoidable leak. The copper leads were chosen as small as consistent with mechanical strength. Further, other avenues of leakage are along the inner glass wall of the neck, and down the column of vapor existing in the latter. The amount of heat leaking along these two paths can be shown by calculation to be very small.

At any rate, the method of experiment was such as to take account of the leakage from the surroundings. Observations of level were taken for at least five minutes with no power input after the calorimeter had been filled and pressure equilibrium attained. When the evaporation of liquid by the current had ceased, readings of the leak were again taken. As was to be expected, the final leak resulted in general smaller than the initial one because of the longer path of conduction down the copper leads to the liquid. The correction to the volume evaporated by the
leak was assumed to be the mean of the initial and final values. It could be maintained that during evaporation the leakage was less than either before or after because of the absorption of some of it by the helium vapors flowing by the wires and the neck of the flask. However, the facts that the velocity of vapor did not reach high values, that the latent heat did not appear to be affected by the rate of evaporation, and that the leak on the average amounted to not more than 1% of the total volume evaporated, appear to show that any error due to the assumption of the mean leak could not be greater than the error in any individual experimental factor.

Since the boiling of the helium under power input is accompanied by the formation of bubbles of vapor, it may be thought that the bursting of these bubbles results in the formation of a considerable quantity of mist and spray which is carried along with the evaporated vapor, the net result being a quantity of liquid removed without any corresponding heat input and a consequent low value of the observed latent heat. Nevertheless, the rate of evaporation was not so great as to cause violent ebullition, and if such effects did occur, it might be expected that they would vary greatly with the rate of evaporation; the results of the latent heat for various rates would appear to show that these effects are negligible.

Since the heating took place at the bottom of the liquid, the formation of bubbles was beneficial in so far as it produced stirring and better uniformity of temperature throughout the liquid. Further, any colder liquid at the top would give rise to convection currents, at least for temperatures higher than that of the maximum density of the liquid.

A height of 6 to 6.5 cm. of liquid usually was evaporated off. Thus the hydrostatic pressure on the lower levels of the liquid varied during evaporation. Because liquid helium is so light, the maximum effect due to this cause at the lowest evaporation pressure, 4 mm. Hg, is 0.3 mm. which is equivalent to about 0.03° K. and which is nearly negligible.

In ascertaining the levels of the liquid, the micrometer eyepiece of the cathetometer telescope served to determine the difference in height between the meniscus and the nearest millimeter mark on the inner wall of the calorimeter. Under the conditions of the experiments, with slight tremors of the helium meniscus due to vibration of compressors, with slight distortion of the meniscus, and with the necessity of taking readings rapidly, it is possible that there may be an error of 0.05 mm. in each meniscus reading, or say, an error of 0.1 mm. for both. The error in volume due to an error in meniscus height may be about 0.5% ; and this is probably the largest single experimental error. Both the power input and time measurement could readily be ascertained with an accuracy of 0.1%.

Method of Operation.

When some liquid helium had been formed in the outer helium flask,
a slight vacuum was produced in the calorimeter, the valve opened, and a current of cold helium vapor passed through to cool off the inner walls of the calorimeter. When liquid covered the valve, it was allowed to flow in. The liquid stood for a few minutes with the proper pressure difference between the inside and outside in order to attain equilibrium and to make sure that any liquid remaining in the copper capillary $D'$ had boiled off. It required but a short time for the latter to occur for the capillary rested in direct thermal contact with the warmer liquid outside. Then the heat leak observations were begun. Between the last reading of the liquid level and the beginning of the current a short time necessarily elapsed during which the level fell slightly. By noting this time interval with the stop watch the exact level at the time of the beginning of the power input was readily ascertained. At the end of the experiment the same procedure held but the correction was somewhat larger and of opposite sign; as a rule, it amounted to less than $0.1\%$ of the volume evaporated.

**Results.**

The results of the experiments are summarized in the table below together with

<table>
<thead>
<tr>
<th>Series</th>
<th>№</th>
<th>Pressure</th>
<th>Temp.</th>
<th>Latent heat of vaporization</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>764 mm.</td>
<td>4°.21 K.</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>496</td>
<td>3.79</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>153</td>
<td>2.96</td>
<td>5.64</td>
</tr>
<tr>
<td>B</td>
<td>I</td>
<td>768</td>
<td>4.21</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>338</td>
<td>3.48</td>
<td>5.56</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>10.4</td>
<td>1.81</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>25.9</td>
<td>2.14</td>
<td>5.58</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>74.3</td>
<td>2.58</td>
<td>5.58</td>
</tr>
<tr>
<td>C</td>
<td>I</td>
<td>211</td>
<td>3.15</td>
<td>5.66</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>108</td>
<td>2.77</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>46.2</td>
<td>2.36</td>
<td>5.47</td>
</tr>
<tr>
<td>D</td>
<td>I</td>
<td>31.7</td>
<td>2.22</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>4.26</td>
<td>1.49</td>
<td>5.45</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>14.5</td>
<td>1.93</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>58.1</td>
<td>2.47</td>
<td>5.59</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>9.04</td>
<td>1.76</td>
<td>5.52</td>
</tr>
</tbody>
</table>
with the important factors entering into the latent heat. The temperatures of the liquid, corresponding to the vapor pressures, were derived from the formula given in Comm. N°. 147b. Densities of the liquid are derived from recent measurements by Kamerlingh Onnes and Boks\(^1\). Because the same kind of glass was used in the construction of the calorimeter as in those experiments, the latent heat results are independent of the value assumed for the coefficient of expansion of the glass in the density measurements. The latent heats are given in 15° calories.

These results are plotted in Fig. 3.

**Discussion of Results.**

From the observations indicated by \(\odot\) it follows that the curve, representing the heat of vaporization as a function of the temperature shows a maximum near 3° K. and descends again at lower temperatures\(^2\). This should support the calculations of Verschaffelt (c.f. Comm. Suppl. N°. 49) who arrives at the conclusion, that at \(T = 0°\) K. the heat of vaporization

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\(^1\) Leiden, Comm. No. 170, p. 22.

\(^2\) Further there is a noteworthy anomaly at the temperature of maximum density. It is possible that only the variation of the state of convection at surpassing this temperature causes a change in a systematic error. The accuracy of the results, however, being sufficient with regard to the deviation with near temperatures, it is remarkable that these results would indicate, that near the maximum density something happens to the helium, which within a small temperature range is perhaps even discontinuous. The change of density of the liquid indicates also something of the same kind.
of helium (solid or liquid) would be about 3.5 cal., and that near the absolute zero the heat of vaporization would change with temperature according to the formula:

\[ L = 3.5 + 1.25 T. \]

The curve, which represents graphically the formula (b) pg. 1059, has been drawn as a dotted line. This formula (b) agrees with the formula given above for small values of \( T \). The joining of the curve of VERSCHAFFELT with the curve of the observations is still giving difficulties.

Our observations, considering the small accuracy of the data for the vapor pressure, agree moderately well with the values \( L \), which can be calculated from the data of MATHIAS, CROMMELIN, KAMERLINGH ONNES and SWALLOW by making use of the formula of CLAPEYRON-CLAUSIUS. One obtains then:

\[
\begin{array}{|c|c|c|c|c|}
\hline
T & \nu_{\text{vap.}} & \nu_{\text{liq.}} & \frac{dp}{dT} & L \\
\hline
3.1 \text{ K.} & 233 & 6.9 & 270 & \pm 5.8 \\
3.5 & 127 & 7.3 & 450 & 6.0 \\
4 & 775 & 7.7 & 640 & 5.7 \\
4.5 & 465 & 8.4 & 870 & 4.0 \\
5 & 26 & 10 & 1110 & 2.8 \\
\hline
\end{array}
\]

These points are also represented in the figure by \( \Delta \).

The values of \( \frac{dp}{dT} \) were calculated from the formula

\[ \log_{10} p = 2.19 - \frac{3.1}{T} + 2.5 \log_{10} T - 0.027 T, \ldots \ldots \quad (1) \]

which was derived from the following reduced formula

\[ \log_{10} \tau = -\frac{0.60}{\tau} + 2.5 \log_{10} \tau + 0.74 - 0.14 \tau, \]

by using \( T_k = 5.19^\circ \text{K.} \) and \( p_k = 2.26 \text{ int. atm. or 1720 mm. Hg.} \).

The reduced formula was obtained by adding to the formula of VERSCHAFFELT (loc. cit.) a correction term, so that for \( T = T_k \) also \( p = p_k \), thus for \( \tau = 1, \tau = 1 \). The formula thus obtained agreed only little less well with the observations than the formula in Leiden Comm. No. 147b; one obtains namely:

\[ \tau < 1 \]

\[ \tau > 1 \]

\[ \tau = 1 \]

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1) Within the limits considered indeed the temperatures, which can be calculated from this formula and from the formula of Comm. No. 147b for a definite value of \( p \), deviate from each other by several hundredths of a degree.
By using the formula:

\[
\frac{d \log p}{dT} = \frac{ML}{RT^2} - \frac{4L}{2T^2} \quad \cdots \quad (a)
\]

one derives from the vapor pressure formula in the neighbourhood of \( T = 0^\circ \text{K} \):

\[ L = 3.5 + 1.25 T - 0.03 T^2 \quad \cdots \quad (b) \]

so that for

\[
\begin{array}{|c|c|}
\hline
T & L \\
\hline
0.5 & 4.1 \\
1.0 & 4.7 \\
1.5 & 5.3 \\
\hline
\end{array}
\]

These points are also represented in the figure by \( \triangle \).

At higher temperatures the simple formula (a) becomes too inaccurate because of the deviations from the gas laws, which the vapor shows. Even at \( \pm 2.5^\circ \text{K} \) these deviations must still be considerable after the isotherm determinations of Kamerlingh Onnes and Boks. One has to apply then the correction, following from the observations of Kamerlingh Onnes and Boks, or when this is no longer satisfactory, one has to calculate at once with the formula of Clapeyron. The specific volume of the saturated vapor, as far as it has not been observed, can then approximately be calculated with the observations in question for some temperatures.

From the values of \( L \) obtained by making use of the formula of

Clapeyron-Clausius, just as from our own observations it seems to follow that the heat of vaporization of helium reaches a maximum at
3.5° K., by which our previous surmise\textsuperscript{1) }is established. Moreover the course of \(L\), so calculated, seems to indicate that also at temperatures lower than 2.5° K. the simple formula (a) is not yet applicable, and that this formula is not valid until immediately near \(T = 0\); this should indicate that, also to lower than 2° K. thus at a reduced temperature lower than 0.4, the behaviour of the saturated vapor of helium deviates still appreciably from the ideal gas laws. However, it could also be possible, that the value of \(L_0\) is another one than was adopted by VERSCHAFFELT.