

NEW MEASUREMENTS ON THE SPECIFIC HEAT OF LIQUID HELIUM

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Summary

Measurements were made on the specific heat of liquid helium under pressure. Moreover new measurements were made on the specific heat of liquid helium under its saturated vapour pressure.

It was ascertained that the principal change in specific heat at the lambda-point occurs within an interval of 0.002 degrees, most probably even within one of 0.0002 degrees.

A superior limit is indicated for the latent heat which might presumably be connected with the transformation occurring at the lambda-point. The smallness of this limit considered in connection with the specific heat corroborates the conclusion which Keesom and Clusius drew from their experiments, that this latent heat is absent.

It appears to be difficult to fix a definite value for the magnitude of the jump of the specific heat at the lambda-point.

The hypothesis is made that the particular shape of the He I branch of the specific heat curve must be ascribed to the influence of fluctuations due to thermal agitation. In connection herewith an argument is derived in favour of the idea that the lambda-transition in liquid helium depends on the interaction between neighbouring atoms.

These considerations concerning the influence of fluctuations are extended to other lambda-phenomena (*e.g.* for ammonium halides, methane, etc.).

From the form of the heating curves the conclusion is drawn that the heat conductivity of liquid helium changes suddenly at the lambda-point.

§ 1. *Introduction.* In § 1 of Comm. No. 216*b*¹⁾ it was mentioned already that measurements of the specific heat of liquid helium under pressure were planned. As it was necessary for that purpose to know the density of liquid helium at given temperature and pressure in order to be able to calculate the amount of liquid helium used in the

1) W. H. Keesom and K. Clusius. Proc. Amsterdam 34, 605, 1931. Comm. Leiden No. 216*b*.

experiments an investigation of the isopycnals of liquid helium was made, the results of which were published in Comm. Nos. 224*d* and *e*¹⁾. The present paper deals with the results of a few measurements of the specific heat of liquid helium at constant volume under pressure.

Moreover, new measurements have been made of the specific heat of liquid helium under its saturated vapour pressure, especially in the vicinity of the lambda-point. In fact, closer investigation of the anomaly in the specific heat of liquid helium ²⁾ gave rise to various questions, thereby showing that new measurements under improved conditions were desirable. As one can see from Fig. 1 of Comm. No. 221*d*, the thermometer, in consequence of the heating element being in its immediate neighbourhood, was strongly superheated during the heating period in the calorimetric experiment. For a closer investigation of what happens during the heating it is therefore desirable to place the heating element as far from the thermometer as possible. So we designed a calorimeter (§ 2) in which the heating coil is located at the bottom, the thermometer being kept in the top part.

A special reason for this arrangement may still be mentioned. In § 3 of the quoted paper attention was drawn to the fact that the after-period of the calorimetric experiment had quite a different aspect above the lambda-temperature from that below (cf. Fig. 1 l.c.). As it was doubted at first whether the density maximum coincides exactly with the jump in the specific heat, an explanation of that sudden change in the aspect of the after-period was looked for in a change of viscosity ³⁾ or of heat conductivity. When, however, it had become clear that the jump in the specific heat is connected with a jump in the expansion coefficient we remarked ⁴⁾ that this might afford the explanation looked for, considering that the expansion coefficient changes from negative in He II to positive in He I. As a matter of fact, since the liquid helium in those experiments was heated from above, convection currents could occur in liquid He II,

1) W. H. Keesom and Miss A. P. Keesom. Proc. Amsterdam 36, 482 and 612, 1933. Comm. Leiden Nos. 224*d* and *e*.

2) W. H. Keesom and Miss A. P. Keesom. Proc. Amsterdam 35, 736, 1932. Comm. Leiden No. 221*d*.

3) We mentioned l.c. that there is probably a change in the viscosity of liquid helium in passing the lambda-point. This change in viscosity has recently been measured by E. F. Burton, Nature 135, 265, 1935.

4) Cf. note 1 p. 24 of Comm. Leiden No. 221*d*.

which would stop immediately on passing the lambda-point. However, in course of time doubts arose as to whether this was the true explanation, and a check became desirable, which could be done by new experiments with heating from below. If convection currents were the real cause the considered effect should then be reversed.

§ 2. *Apparatus.* The method was the same as the one used for the measurements of Comm. No. 221*d*. In the apparatus the following alteration was made.

In order to heat the liquid helium from below (cf. § 1) a supplementary core (*E*, fig. 1) with a constantan heating wire *F* was introduced in the bottom of the calorimeter. Using this heating element has the advantage that, if at all, the thermometer is superheated to a much smaller degree. And indeed the temperature equilibrium appeared to be restored in He I within 1 minute after heating was stopped (in our previous experiments in about 4 minutes). In He II the same occurred within 10 seconds. *D* is a copper cross for better conducting the heat into the liquid.

The volume of the calorimeter, measured volumetrically, was 73.26 cm^3 at room temperature, hence¹⁾ 72.57 cm^3 at liquid helium temperatures.

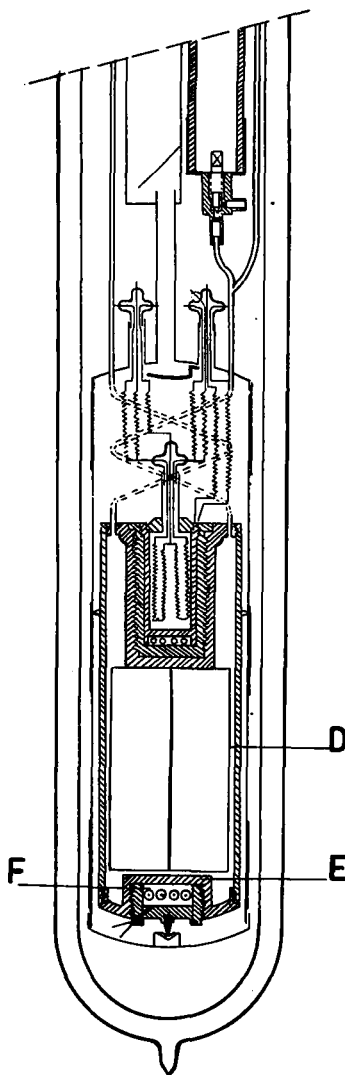


Fig. 1. Calorimeter with heating core below.

1) Expansion coefficient of copper: W. H. Keesom, F. P. G. A. J. van Agt and Miss A. F. J. Jansen, Comm. Leiden No. 182*a*.

The density of the liquid helium was calculated from temperature and pressure by means of the data published in Suppl. No. 76b¹⁾.

§ 3. *The results* have been collected in Tables I and II, and are represented in figs. 2 and 3. Temperatures are given on the 1932 scale, putting the lambda-point at 2.1900°K.

TABLE I

| Specific heat of liquid helium under its vapour pressure. Measurements of Dec. 21, 1934. | | | | | | | | |
|---|---------------|------------------|----------------------------|--------------------------|---------------------|-----------------------------|------------------------------------|-----------------------------------|
| No. | Current mA | Tension Volts | Heating time seconds | Heat supplied cal. | Temper- ature °K | Temp. increase degree | Heat capacity cal/ degree | Spec. heat cal/g. degree |
| Ia | 14.68 | 0.759 | 60 | 0.1618 | 1.231 | 0.1595 | 1.014 | 0.1001 |
| Ib | 14.68 | 0.759 | 60 | 0.1618 | 1.224 | 0.1730 | 0.935 | 0.0923 |
| Ic | 14.66 | 0.759 | 60 | 0.1616 | 1.314 | 0.1136 | 1.422 | 0.1404 |
| Id | 14.66 | 0.760 | 60 | 0.1618 | 1.487 | 0.0574 | 2.810 | 0.278 |
| Ih | 16.06 | 0.833 | 60 | 0.1942 | 2.041 | 0.0143 | 13.58 | 1.34 |
| Ij | 16.06 | 0.835 | 60 | 0.1946 | 2.069 | 0.0132 | 14.70 | 1.45 |
| Im | 16.12 | 0.839 | 60 | 0.1962 | 2.105 | 0.0118 | 16.56 | 1.63 |
| Io | 16.08 | 0.839 | 60 | 0.1958 | 2.131 | 0.0108 | 18.09 | 1.79 |
| Iq | 16.04 | 0.831 | 60 | 0.1934 | 2.149 | 0.0098 | 19.78 | 1.95 |
| Is | 16.04 | 0.833 | 60 | 0.1939 | 2.168 | 0.0083 | 23.25 | 2.29 |
| It | 16.04 | 0.833 | 60 | 0.1939 | 2.177 | 0.0075 | 25.85 | 2.55 |
| Iu | 16.04 | 0.831 | 60 | 0.1934 | 2.184 | 0.0066 | 29.16 | 2.88 |
| Iv | 16.04 | 0.833 | 60 | 0.1939 | 2.188* | 0.0033 | 59.12 | 5.83 |
| Iw | 16.03 | 0.831 | 60 | 0.1933 | 2.197* | 0.0156 | 12.42 | 1.226 |
| Ix | 16.03 | 0.833 | 60 | 0.1938 | 2.213 | 0.0203 | 9.57 | 0.945 |
| Iy | 16.02 | 0.833 | 60 | 0.1937 | 2.232 | 0.0223 | 8.31 | 0.819 |
| Iz | 16.00 | 0.831 | 60 | 0.1930 | 2.253 | 0.0255 | 7.56 | 0.746 |
| Iα | 15.96 | 0.831 | 60 | 0.1925 | 2.276 | 0.0277 | 6.96 | 0.687 |
| IIg | 8.68 | 0.500 | 60 | 0.0622 | 2.173 | 0.00259 | 24.1 | 2.37 |
| IIh | 8.67 | 0.499 | 60 | 0.0620 | 2.176 | 0.00248 | 25.0 | 2.46 |
| IIi | 8.68 | 0.499 | 60 | 0.0622 | 2.179 | 0.00244 | 25.5 | 2.51 |
| IIj | 8.68 | 0.500 | 60 | 0.0622 | 2.181 | 0.00231 | 26.9 | 2.65 |
| IIk | 8.67 | 0.500 | 60 | 0.0622 | 2.183 | 0.00222 | 27.9 | 2.75 |
| IIl | 8.67 | 0.500 | 60 | 0.0622 | 2.186 | 0.00209 | 29.7 | 2.93 |
| IIm | 8.67 | 0.500 | 60.5 | 0.0627 | 2.188* | 0.00192 | 32.6 | 3.21 |
| IIn | 8.67 | 0.500 | 60.4 | 0.0626 | 2.190* | 0.00207 | 30.2 | 2.97 |
| IIo | 8.65 | 0.500 | 60.4 | 0.0624 | 2.194 | 0.00423 | 14.8 | 1.45 |
| IIp | 8.67 | 0.500 | 60.9 | 0.0631 | 2.198 | 0.00525 | 12.0 | 1.18 |
| IIq | 8.68 | 0.500 | 60.6 | 0.0629 | 2.203 | 0.00554 | 11.3 | 1.12 |
| IIr | 8.68 | 0.500 | 60.9 | 0.0632 | 2.208 | 0.00601 | 10.5 | 1.03 |

The amount of liquid helium was 10.131 g for series I and 10.153 g for series II.
The measuring current was 1.31 mA.

In fig. 2 we see that the shape of the curves of the specific heat at constant volume is very much the same as that of liquid helium under its vapour pressure. For liquid helium II the specific heat at

1) W. H. Keesom and Miss A. P. Keesom. *Physica* 1, 128, 1933—1934. Comm. Leiden Suppl. No. 76b.

constant volume is larger than that under vapour pressure and becomes larger as the pressure and density increase. For liquid helium I the c_v is smaller than the c_s and becomes smaller with increasing pressure and density. At the lambda-point we see a jump which seems to be smaller than the jump in the c_s . Just above the lambda-point we see as in the case of the c_s a rather steep decrease of the c_v , followed by a slow increase.

TABLE II

| Specific heat of liquid helium at constant volume. Measurements of Januari 11, 1935. | | | | | | | | |
|--|---------------|------------------|----------------------------|--------------------------|---------------------|-----------------------------|------------------------------------|-------------------------------------|
| No. | Current mA | Tension Volts | Heating time seconds | Heat supplied cal. | Temper- ature °K | Temp. increase degree | Heat capacity cal/ degree | Specif. heat cal/g. degree |
| Ic | 15.46 | 0.795 | 60 | 0.1786 | 1.734 | 0.01267 | 14.09 | 1.109 |
| Ig | 15.46 | 0.795 | 60 | 0.1786 | 1.768 | 0.01171 | 15.25 | 1.201 |
| Ii | 15.49 | 0.797 | 60 | 0.1794 | 1.790 | 0.01112 | 16.13 | 1.270 |
| Ik | 15.49 | 0.797 | 60 | 0.1794 | 1.811 | 0.01040 | 17.24 | 1.357 |
| Im | 15.49 | 0.797 | 60 | 0.1794 | 1.831 | 0.00932 | 19.24 | 1.515 |
| In | 15.49 | 0.797 | 60 | 0.1794 | 1.838 | 0.00857 | 20.93 | 1.648 |
| Io | 15.55 | 0.799 | 60 | 0.1805 | 1.846 | 0.00725 | 24.90 | 1.960 |
| Ip | 15.55 | 0.799 | 68 | 0.2046 | 1.857 | 0.01921 | 10.65 | 0.839 |
| Iq | 15.55 | 0.799 | 60 | 0.1805 | 1.873 | 0.02514 | 7.179 | 0.565 |
| Ir | 15.55 | 0.799 | 60 | 0.1805 | 1.921 | 0.03978 | 4.539 | 0.357 |
| Is | 15.55 | 0.799 | 60 | 0.1805 | 1.952 | 0.04117 | 4.384 | 0.345 |
| It | 15.55 | 0.797 | 60 | 0.1800 | 1.997 | 0.03969 | 4.536 | 0.357 |
| Iu | 15.55 | 0.799 | 60 | 0.1805 | 2.081 | 0.04689 | 3.849 | 0.307 |
| Iw | 15.55 | 0.799 | 60 | 0.1805 | 2.129 | 0.04816 | 3.748 | 0.295 |
| | | | | | | | | |
| IIa | 15.46 | 0.795 | 60 | 0.1786 | 1.211 | 0.09553 | 1.869 | 0.153 |
| IIb | 15.49 | 0.795 | 60 | 0.1889 | 1.391 | 0.04596 | 3.893 | 0.319 |
| IIc | 15.27 | 0.783 | 60 | 0.1737 | 1.728 | 0.01688 | 10.29 | 0.843 |
| IId | 15.43 | 0.791 | 60 | 0.1737 | 1.870 | 0.01195 | 14.84 | 1.215 |
| IIe | 15.46 | 0.793 | 60 | 0.1781 | 1.910 | 0.01047 | 17.01 | 1.393 |
| IIf | 15.49 | 0.795 | 60 | 0.1789 | 1.925 | 0.00992 | 18.03 | 1.476 |
| IIg | 15.40 | 0.791 | 60 | 0.1770 | 1.950 | 0.00895 | 19.77 | 1.619 |
| IIh | 15.37 | 0.789 | 60 | 0.1762 | 1.959 | 0.00832 | 21.18 | 1.734 |
| IIi | 15.37 | 0.789 | 60 | 0.1762 | 1.965 | 0.00740 | 23.81 | 1.949 |
| IIj | 15.40 | 0.791 | 60 | 0.1770 | 1.978 | 0.01288 | 13.74 | 1.125 |
| IIk | 15.24 | 0.779 | 60 | 0.1725 | 2.006 | 0.02810 | 6.139 | 0.503 |
| IIl | 21.71 | 1.122 | 60 | 0.3537 | 2.119 | 0.07383 | 4.791 | 0.392 |
| IIm | 36.3 | 1.884 | 60 | 0.993 | 2.448 | 0.2292 | 4.333 | 0.355 |
| IIx | 36.3 | 1.886 | 60 | 0.995 | 2.784 | 0.2195 | 4.533 | 0.371 |
| Ily | 36.3 | 1.884 | 60 | 0.993 | 3.139 | 0.2070 | 4.797 | 0.393 |
| IIz | 36.2 | 1.884 | 60 | 0.990 | 3.437 | 0.1935 | 5.115 | 0.419 |
| IIα | 36.2 | 1.884 | 60 | 0.990 | 3.744 | 0.1911 | 5.180 | 0.424 |
| IIβ | 36.2 | 1.884 | 60 | 0.990 | 3.991 | 0.1804 | 5.489 | 0.449 |
| IIγ | 36.3 | 1.886 | 60 | 0.995 | 4.282 | 0.1790 | 5.560 | 0.455 |
| For series I the density of liquid helium was 0.1750, for series II 0.1683 g/cm ³ . Measuring current was 1.31 mA. | | | | | | | | |

§ 4. *The lambda-point.* a. In § 4a of Comm. No. 221d we concluded that the specific heat of liquid helium (under its saturated vapour

pressure) falls at about 2.19°K from a value of 3.0 to a value of about 1.1 within a temperature interval which is certainly not more than 0.02 degrees, very probably even not more than two thousandths of a degree. The measurements now made on liquid helium under its saturated vapour pressure (table I) allow us to fix the limits of the temperature interval within which the fundamental change in specific heat takes place considerably more closely.

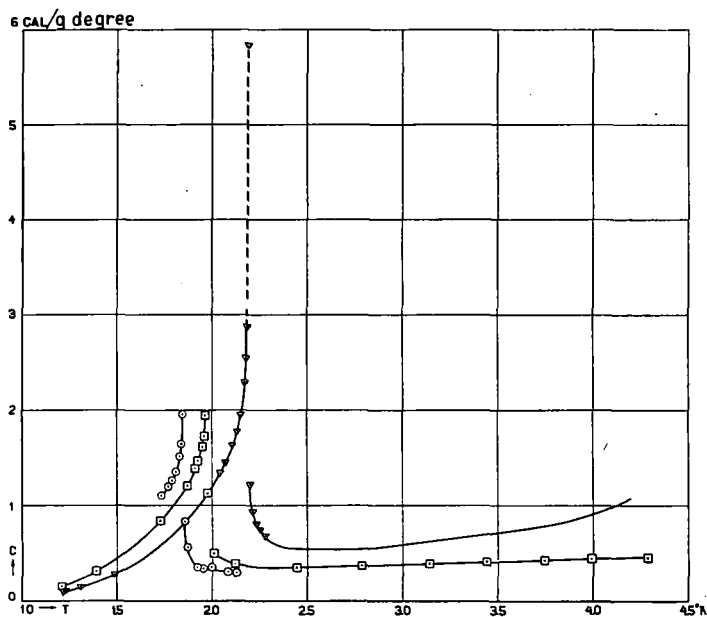


Fig. 2. Specific heats of liquid helium.

▽ 21st Dec. 1934. Series I. Helium under saturated vapour pressure.

○ At about 25 atm. } 11th Jan. 1935. Constant volume.
 □ " " 19 " }

In fig. 4 the galvanometer readings of the points Iu , v and w of table I have been plotted.

Comparing the temperature increases and considering that the heat supplied was very nearly the same in all three cases we are immediately struck by the great change that occurs in the specific heat.

In Iv 21st Dec. the lambda-point was passed between points 4 and 5 (cf. description under Fig. 4). This fixes the position of the lambda-point to 0.002° degree. In other measurements in which the passing

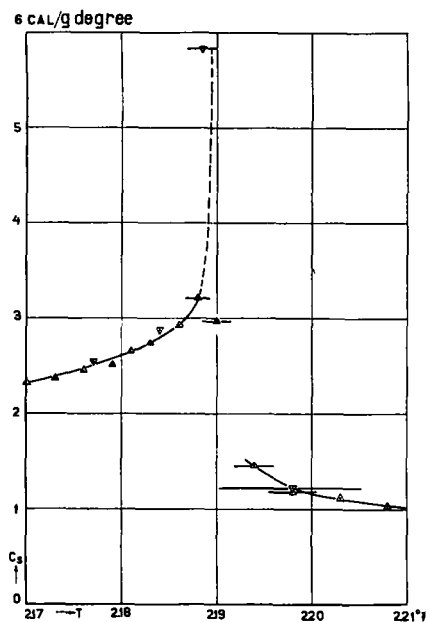


Fig. 3. Specific heats of liquid helium under its saturated vapour pressure in the neighbourhood of the lambda-point.

▽ Series I with Diesselhorst galvanometer.
 △ " II " Zernike "

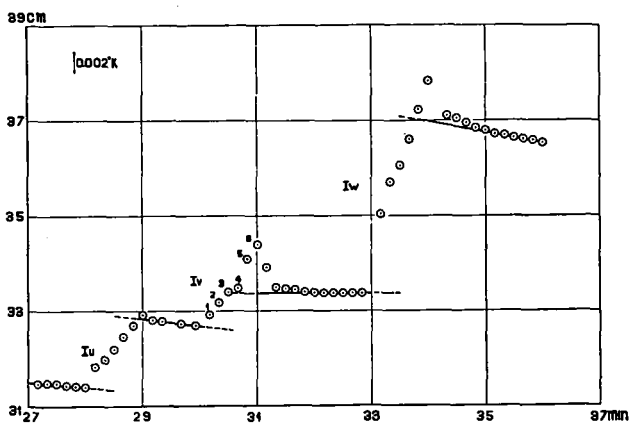


Fig. 4. Galvanometer readings of calorimetric experiments with liquid helium. The observer noted that in Iv the lambda-point was passed ¹⁾ at 30^m42^s.

1) Made evident by a sudden acceleration of the galvanometer, after having slowed down before.

of the lambda-point occurred, this fact was not especially noted. From a discussion of the galvanometer readings it can, however, be deduced between which readings it must have occurred. A similar criterium as used for *Iv* then gives:

21st Dec. *II**n*: 0.001⁷ degree,
 11th Jan. *I**o*: 0.003⁶ "
 " " *II**t*: 0.001⁸ " 1).

We conclude that by this criterium the position of the lambda-point is fixed to about 0.002 degree.

We can, however, obtain a still more definite result by a closer inspection of experiment *Iv* of the 21st of Dec. From what was observed during the heating as well as from the after-period we conclude that point 4 of the diagram in Fig. 4 coincides, or very nearly so, with the lambda-point. The difference of 1 mm of scale in the reading of the point in the heating period and the same point in the after-period (indicated by an angle in the curve) is due to a small temperature difference between the wall of the calorimeter and the neighbouring liquid during the heating. We accept that the position of the lambda-point can be fixed to about 0.5 mm reading on the scale. This comes to 0.0002 degree.

We conclude that the large change in specific heat occurs either abruptly or in a temperature interval most probably smaller than about 0.0002 degree.

b. The question whether any latent heat is still left connected with the lambda-transformation can be best discussed from measurement *II**n* of 21st Dec. (Fig. 5). The heat supplied was 0.00626 cal/g. Temperature increase 0.00207 degree. Comparison of the readings of the galvanometer with those of the preceding and the following measurements show that the lambda-point certainly lies between points 1 and 3, probably near to 2, very likely not more than 0.0001 degree below 2, *i.e.* 0.00038 degree above the temperature at the beginning of the heating. Accepting the latter figure, and subtracting 0.00038×3.2 cal/g for the heat supply during the He *II* period, and 0.00169×1.8 for the He *I* period, 0.00188 cal/g is left as a maximum limit of the latent heat. The smallness of this maximum limit is apparent when we realize that it corresponds to a heating of *e.g.* He *I* quite near the lambda-point over an interval of about 0.001 degree.

1) The result of the discussion of this particular point is somewhat uncertain.

We feel sufficiently justified in assuming that these results corroborate the conclusion drawn by Keesom and Clusius¹⁾ from their experiments, *viz.* there is no latent heat connected with the lambda-transformation in liquid helium.

c. On the magnitude of the jump in the specific heat.

α . We consider first the jump of the specific heat of liquid helium under its saturated vapour pressure. One difficulty in assigning a definite value to it arises from the fact that the result depends essentially on the assumption concerning the absence or existence of a latent heat (cf. sub *b*). If the conclusion is accepted that a latent heat is absent, experiment Iw (21st Dec.) indicates that the maximum value of c_s most probably lies a good deal above 6.0 cal/g. We must

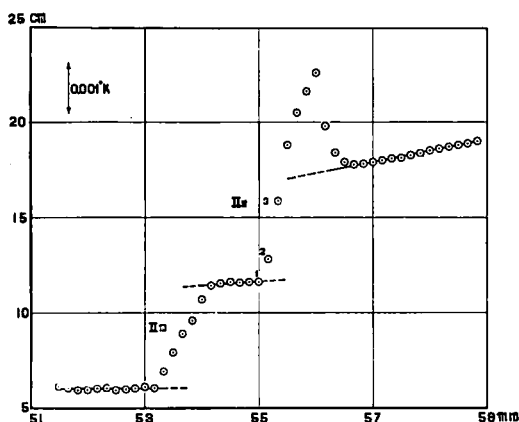


Fig. 5. Measurements of specific heat of liquid helium (21 Dec. 1934).

not forget, however, that this conclusion depends on the result of one experiment only.

An acceptable extrapolation (over 0.004 degree) of the He I branch points to a limiting value of about 1.8 for He I.

From experiments II m and o of 21st Dec. it follows with certainty that c_s changes from 3.21 to 1.45 in an interval of 0.006 degree.

β . As for the measurements of c_v of liquid helium under pressure we may remark that they were not intended as a closer investigation as to the true nature of the lambda-transformation. The temperature increases were taken somewhat larger than for the measurements

1) W. H. Keesom and K. Clusius. Proc. Amsterdam 35, 307, 1932. Comm. Leiden No. 219e.

under the saturated vapour pressure. We can therefore derive from them only rather inferior limits for the jump in the specific heat. These are:

at 24.1 atm. (exp. I₀ and *p* 11th Jan.): from 1.960 to 0.839 = 1.121
in 0.009 degree,

at 16.8 „ (exp. II_s and *u* 11th Jan.): from 1.949 to 0.503 = 1.446
in 0.041 degree.

As I₀ overlaps the lambda-point the maximum for He II is decidedly appreciably larger than 1.960, the jump therefore appreciably larger than 1.121.

§ 5. *a.* When we consider the data collected in § 4*c* from which we should like to obtain some idea of the magnitude of the jump in the specific heat, it strikes us as being very difficult to assign a definite value to it. The result depends largely on how near the mean temperatures of the last measurement below, and of the first measurement above, the lambda-point are to this point. A look at fig. 2, especially at the curve for the specific heat of liquid helium under its saturated vapour pressure, explains this point. One might even be inclined to presume that also the He I branch in the immediate neighbourhood of the lambda-point rises very steeply to rather high values. The difference, however, remains, that this ultimate rapid rise, if it really exists for He I, occurs in a still appreciably smaller temperature interval, than does the rise of the He II-branch. The specific heat curve is definitely assymetric at the lambda-point.

b. On considering the shape of the He II-branch of the specific heat curve the idea suggests itself that in He II a process is obviously going on that causes first a gradual, then an accelerated increase of the specific heat with rising temperature, which increase suddenly comes to an end at the lambda-point. If we compare with that the shape of the He I branch just above the lambda-point, especially if we do so in the light of what has been pointed out under *a*, we are led to the idea that what occurs in He I seems to be of a secondary nature, dependent on what happens in the He II condition. So the question arises whether that particular shape of the He I branch might not be a consequence of the existence of fluctuations in the liquid. If the overall temperature of the liquid is some thousandths of a degree above the lambda-point we must expect in the liquid a certain number of volume-elements in which the local temperature

is below the lambda-point, and in which the liquid helium is in the II condition. If these parts should give a perceptible contribution to the specific heat, this constant ought to be found larger than corresponds to the He I-condition properly.

The following rough estimate seems to corroborate this idea.

We suppose that we can divide the total mass of the liquid in n volume-elements, each with mass μ , $n\mu = 1$, in such a way that in each of these volume-elements the condition of the liquid can be regarded as uniform. We assume the specific heat of He I to be constant: $\beta = 0.5$. We assume the specific heat of the He II as far as it is present also to be constant: $\alpha = 6.0$.

Let there be $0.1 n$ volume-elements in which the liquid helium is in the II-condition. The mean specific heat is then 1.05 ¹⁾. This is the case (for helium under saturated vapour pressure) at $\tau = T - T_\lambda = 0.014$.

The probability of a volume-element being just in the He II-condition is given by the expression $\exp(-\mu\beta\tau^2/2kT_\lambda^2)$. This is equal to 0.1 for $\mu = 5 \times 10^{-19}$, i.e. for each volume-element containing about 10^5 atoms.

The last number is necessarily very inexact for various reasons. Nevertheless we think we may draw from the above estimate, however rough it may be, the following conclusions:

α . the rapid increase of the He I branch of the specific heat curve of liquid helium can be explained by considering the fluctuations due to thermal agitation;

β . the lambda-transition in liquid helium is not an atomic phenomenon, but depends on the interaction between a certain, of course not very definite, number of neighbouring atoms (a kind of correlation effect).

The last mentioned conclusion leads us back to the considerations concerning the nature of the He II-condition given by one of us in Comm. Leiden Suppl. No. 71e, § 2.

c . The following remarks may be added.

α . The He II branch of the specific heat curve will also suffer a fluctuation effect. As a consequence, the ascent of the specific heat curve will be less steep than would be the case if no fluctuation

1) Here we calculate as if, in heating, the considered volume-elements remain intact and simply join in with their particular heat capacity. This assumption of course cannot be more than a very rough approximation to reality.

occurred. This points to the fact that the jump in the specific heat connected with the lambda-transition proper (*i.e.* considered for a number of duly correlated atoms) would be still more prominent than is revealed by actual experiment.

β . Obviously the same explanation as put forward here for the particular shape of the He I branch of the specific heat curve can be tried for the corresponding branches of the specific heat curve for other substances such as ammonium halides, methane, etc. which show the lambda-phenomenon. In this way these considerations can be connected with Fowler's¹⁾ deductions in which Pauling's conception of a transition of certain atom groups from the vibrational to the rotational stage, together with the assumption of a correlation effect (cf. under $b\beta$) promoting their transition, form the bases of a theory of the lambda-transformation for such substances.

By introducing this correlation effect they go farther than did Brody's²⁾ remarks on an influence of thermal fluctuations on the specific heat of a solid below its melting point. There, in fact, such a correlation effect seems to play no part. In the liquid state a corresponding effect near the solidification point is not to be expected, as, obviously, thermal agitation does not give rise to the formation of crystals to any considerable extent unless at temperatures appreciably below that point³⁾.

§ 6. *On heat conduction in liquid helium.* From figs. 4 and 5 it is clear that also in the experiments now carried out with heating from below there is a marked difference between the after-periods below and above the lambda-point. Fig. 6, which gives a longer part of a series of measurements, shows this difference still more markedly. It is very striking that the change in the shape of the after-period takes place at once in passing the lambda-point. We observe that for temperatures below the lambda-point the heat exchange in the calorimeter takes place again very rapidly, whereas above the lambda-point it takes some time (cf. also § 2). Above the lambda-point the thermometer appears to be markedly superheated, below

1) R. H. Fowler Proc. Roy. Soc. A 149, 1, 1935.

2) E. Brody. Physik. Zs. 23, 197, 1922.

3) Considerations concerning the consequences of the fluctuation effect for the magnetisation curves and for the specific heat of ferromagnetic substances in the neighbourhood of the Curie-point were made by L. Néel, Ann. de Phys. 18, 5, 1932. Journ. de Phys. (7) 5, 104, 1934.

the lambda-point the superheating of the thermometer is only small. The reversal of the effect mentioned at the end of § 1 does not occur. We conclude that it is not the reversal of the sign of the expansion coefficient that causes the change of shape of the after-period curves on passing the lambda-point.

One might think that the abrupt increase of the viscosity (cf. p. 559, note 1) in passing the lambda-point could cause a corresponding decrease of the intensity of the convection currents resulting in a sudden decrease of the heat exchange. As, however, at these experiments, notwithstanding the heating from below, the thermometer

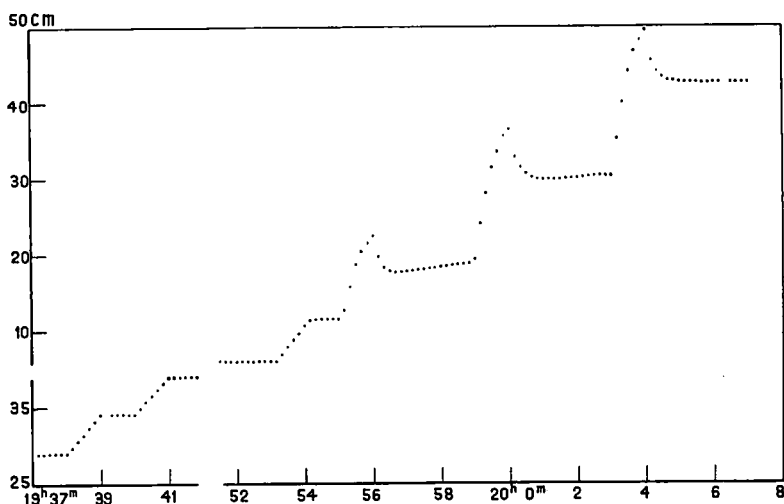


Fig. 6. A series of calorimetric experiments on liquid helium, showing the difference in shape of the after-periods.

has a temperature higher than that of the liquid helium, so that the whole wall has a temperature higher than the liquid within, we presume that convection currents do not occur at all to a noticeable degree.

We conclude that these experiments show that there is also a sudden change in the heat conductivity when passing from He II to He I. From estimates of the degree of superheating of the thermometer as derived from the heating curves below and above the lambda-point we presume that this change in the heat conductivity is rather important. Measurements on this point are in the course of being prepared.

X-RAY EVIDENCE ON THE IONIC ARRANGEMENT IN THORIUM NITRATE SOLUTIONS

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(Communication from Natuurkundig Laboratorium der Rijks-Universiteit te Groningen)

Summary

A quantitative study is made of the diameter of the diffraction halo with thorium nitrate solutions of different concentrations. The results are best accounted for by ascribing the principal halo to the arrangement of Th-ions. This arrangement is more regular than would follow from the available free space. If the ions are assumed to be heavily hydrated so as to form more or less a close-packed arrangement, good agreement with the experimental results is obtained. A less closely packed arrangement of the Th-ions (e.g. of the simple cubic or tetrahedral type) would give a less satisfactory agreement.

Only a few cases ¹⁾ ²⁾ are known in which the X-ray diffraction pattern of a solution shows a halo, the diameter of which varies with concentration, in such a way as to ascribe it to the *distance* between the *solute* molecules (or ions). Thorium nitrate in water appears to exhibit this phenomenon the most clearly, the halo being still visible at a concentration of less than 1 mole: 200 moles. So we have investigated this case more closely in the hope of deriving from it the arrangement of the Th^{++++} -ions in the liquid.

"Dry" thorium nitrate from Brocades and Stheeman (Meppel) was used. An analysis kindly performed by dr. Bottema of the laboratory for anorganic chemistry in Groningen gave within 1% the constitution $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. Solutions of different concentrations were examined by the reflexion method. The instrumental arrangement was: diameter spectrograph 5,6 cm, scattering surface about 2 cm long, slit $1,6 \times 0,2 \text{ mm}^2$, glancing angle 2° — 3° , small focus, Cu-radiation filtered by $10 \mu \text{ Cu}$ before

1) P. Krishnamurti, Ind. J. Phys. **3**, 209, 1929.

2) J. A. Prins, Physica **1**, 1171, 1934; J. chem. Phys. **3**, 72, 1935.

the slit and $15\ \mu$ Ni before the film, 6 hours exposure, 15 kV, 15 mA.

Fig. 1 gives an idea of the photographs; in the originals the ring is a little more pronounced.

As the concentrations of the solutions were known (the components having been weighed) and as the densities were determined, we are able to calculate the number of Th-ions per cm^3 in each case. From this a certain "mean distance between neighbouring Th-ions" may be calculated. We used the formula ¹⁾:

$$d = 0,814 \cdot 1,33 \sqrt[3]{M/D} \quad (1)$$

Here M is the molecular weight of $\text{Th}(\text{NO}_3)_4 + n\ \text{H}_2\text{O}$ (n being the *total* number of water molecules present per $\text{Th}(\text{NO}_3)_4$ molecule), D is the density measured, d is the „spacing" in Å. It is compared in

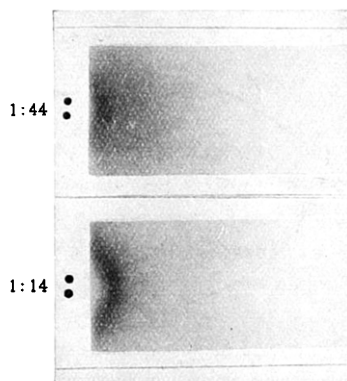


Fig. 1. Diffraction patterns of 1 : 14 and 1 : 44 molal solutions $\text{Th}(\text{NO}_3)_4 : \text{H}_2\text{O}$.

fig. 2 with the experimental "spacing" calculated from the diffraction angle 2φ of the maximum of the halo by Bragg's relation:

$$\lambda = 2d \sin \varphi \quad (2)$$

The diffraction angles were determined by comparison with spectra from a layer of palmitic acid substituted for the surface of the liquid. The results are summarised in Table I.

1) W. H. Keesom and J. de Smedt, Proc. Amsterdam **25**, 118, 1922; J. A. Prins, Z. f. Phys. **56**, 617, 1929. See also footnote on following page.

TABLE I

| | | | | | | | |
|---------------------------------------|----------|----------|----------|----------|----------|----------|----------|
| Molal concentration . . . | 1 : 13,9 | 1 : 19,0 | 1 : 22,6 | 1 : 30,1 | 1 : 44,4 | 1 : 69,1 | 1 : 84,0 |
| Density | 2,04 | 1,84 | 1,76 | 1,59 | 1,44 | 1,31 | 1,26 |
| $\frac{1}{2}$ diffraction angle . . . | 5°57' | 5°06' | 4°32' | 4°23' | 4°12' | 3°38' | 3°25' |
| Spacing from (2) in Å . . | 7,4 | 8,6 | 9,5 | 10,0 | 10,5 | 12,1 | 12,9 |
| Spacing from (1) in Å . . | 7,67 | 8,25 | 8,60 | 9,53 | 10,4 | 11,7 | 12,6 |

As is well known ¹⁾, formula (1) corresponds to the assumption of a „close-packed” arrangement of Th-ions (each surrounded by water). If another arrangement is used, where every „ion + its water” has less than 12 equivalent neighbours, the agreement with experimental data is less good. Especially arrangements with 4 neighbours (as in diamond) or 6 (simple cubic) appear to be excluded (except perhaps for concentrations around 1 : 25).

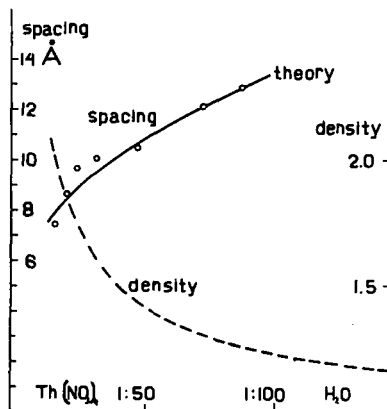


Fig. 2. Spacing (exp. circles and theor. curve) and density for different molal proportions $\text{Th}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$

These results *may* be interpreted as follows: The Th-ions draw all the water molecules around them. These „hydrated ions” form a liquid close-packed arrangement, the NO_3 -ions finding place somewhere between.

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1) See note 1 page 571. Throughout the text the more suggestive terms „arrangement” and „spacing” are used to indicate the more accurate conceptions „distribution function for the interionic distance” and „its (principal) period”.