

Physics. — *The melting-curve of helium and the heat-theorem of NERNST.* By W. H. KEESOM ¹⁾. (Supplement N^o. 61b to the Communications from the Physical Laboratory at Leiden).

(Communicated at the meeting of March 26, 1927).

§ 1. In the proceedings of the meeting of January 29, 1927 ²⁾ it appears that Dr. VAN LAAR objects to a passage in my Communication about the solidification of helium ³⁾, which passage concerns a relation between the course of the melting-curve and the heat-theorem of NERNST. This prompts me to give a more detailed explanation of the point in question. Further I will confine myself to two remarks on the case maintained by Dr. VAN LAAR.

§ 2. *What do the measurements concerning the melting-curve of helium teach about the heat-theorem of NERNST?*

I presuppose that we don't know anything about the course of the melting-curve of helium below 1° K. as long as we are in want of experimental data about that ⁴⁾. A course such as Dr. VAN LAAR gives, that is to say with a minimum at about 1° K., after that rising again at a diminishing temperature, to be tangent to the *p*-axis at 0° K., I don't think this to be impossible. But I don't think this course probable. Already the plain consideration of the part of the melting-curve known from the experiments (see Comm. N^o. 184b Fig. 2) rouses as regards the continuation to the lower temperatures an expectation of going more and more parallel with the *T*-axis, rather than a bending in the sense of Dr. VAN LAAR.

In order to be able to criticize this more objectively two of my assistants have each noted down at my request the pressure of each 0.1 degree of a smooth curve (two curves drawn independently) of 1.2 to 3° K., which as much as possible corresponds with the points of observation, have divided these pressures in two series of readings for values of *T*, which again and again differ 0.2 degree and have made up the second differences in these series.

Thus for each 0.1 degree was found an approximate value of $\frac{d^2p}{dT^2}$. The results are given in Fig. 1. Striking is the acute maximum at

¹⁾ Abridged translation.

²⁾ J. J. VAN LAAR, *These Proceedings* 30, 244.

³⁾ *These Proceedings* 29, 1136. Comm. Leiden N^o. 184b.

⁴⁾ Except of course that it does not meet with the vapour-pressure-curve at the lowest temperature reached by KAMERLINGH ONNES and valued at 0.82° K.

1.8⁵⁰ K. and the steep declining of the curve at lower temperatures.

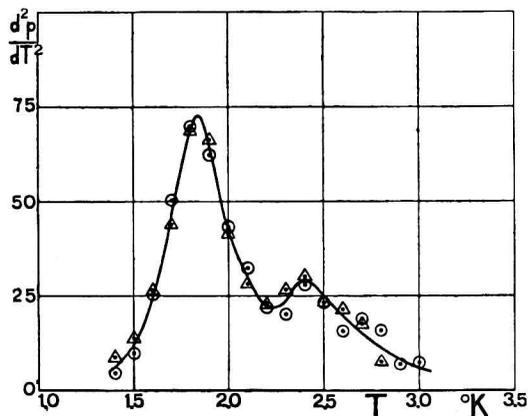


Fig. 1.

The latter is not in any part in keeping with that which Dr. VAN LAAR should wish.

According to Dr. VAN LAAR at a sufficiently low temperature $\frac{d^2p}{dT^2}$ should be proportional to T^{-1} and so the curve for $\frac{d^2p}{dT^2}$, at diminishing temperature, should rise asymptotically to the p -axis. As the diminishing of $\frac{d^2p}{dT^2}$ between 1.8°

and 1.4° K. will have to be considered as fixed by experiment, then according to Dr. VAN LAAR, the curve for $\frac{d^2p}{dT^2}$ should make a sharp bend upwards to the left. It is evident that experiment does not give any reason to think this probable in any way¹⁾.

For the sake of clearness — perhaps unnecessarily — I have put a formula of the form

$$p = aT \log T + \beta T + \gamma,$$

as Dr. VAN LAAR thinks probable (p. 248 l.c.) through the points 1.2°, 1.8° and 2.4° K. of one of the two drawn curves mentioned before corresponding as closely as possible to the observations.

The result was: $p = 168,4 T \log T - 95,32 T + 123,72$. On Fig. 2 this curve (dotted line) has been drawn together with the experimental curve (drawn line). The deviations greatly exceed the experimental inaccuracy. Meanwhile it may be observed that it is perhaps not allowed to treat the coefficients a , β and γ as constants, that on the contrary they themselves must still be considered as temperature-functions. I should like to have this figure regarded only as an illustration of the fact, that the experimental curve has not at all the course of a curve,

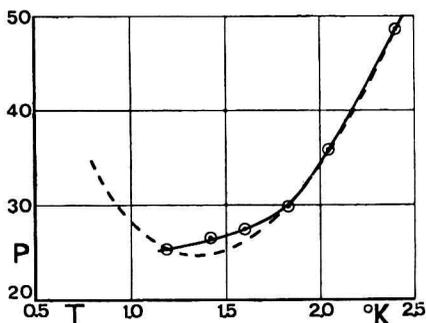


Fig. 2.

¹⁾ I should not like to assert that the second top in the curve at 2.3° K. is real. It could be the consequence of the way of drawing the p, T curves. Meanwhile it is remarkable that both the assistants find this top and that it coincides with the place of the maximum of density of the liquid, see KAMERLINGH ONNES and BOKS, Leiden, Comm. N^o. 170b, § 4.

which goes through a minimum and after that will again strongly rise to the left, as Dr. VAN LAAR expects to be the case.

Inferring from this, I think that as the most probable continuation of the experimental curve to temperatures below $1^{\circ}.2$ K, may be accepted a curve declining with a small bend. We may further accept that the curve will meet the p -axis at last with a horizontal tangent or that the curve still keeps a small inclination ¹⁾).

If we now pass on the question, what follows from this in connection with the heat-theorem of NERNST, then we must keep the two possibilities just mentioned strictly apart. Perhaps it is a good thing to state here once more distinctly, that in both cases we bring about an extrapolation. Without extrapolation, however, nothing can be said about the theorem of NERNST. For the rest the region of temperature, over which the extrapolation extends itself here, is, expressed in degrees, many times smaller than with any other equilibrium examined in this sense, though with this we don't want to say that this last degree, which still separates us from absolute zero, might not still give extraordinary surprises. We must particularly leave open the possibility that between $1^{\circ}.2$ and 0° K. might still take place a transformation in the solid phase. However we here leave this possibility out of regard.

a. Let us then in the first place consider the case that $\frac{dp}{dT}$ for the melting-curve should approach to 0 at $T=0$. If we write the equation of CLAPEYRON in the form:

$$\frac{dp}{dT} = \frac{S_{liq} - S_{sol}}{v_{liq} - v_{sol}},$$

then follows that for $T=0$, S_{liq} should be $= S_{sol}$. and so the entropies of the zero-point for the solid and liquid phase would be equal for helium. This then would be in strict correspondence with the heat-theorem of NERNST.

b. However if we accept that the melting-curve on approaching $T=0$ still keeps a small inclination and also, what seems probable, that $v_{liq} - v_{sol}$, though this difference is small (see Comm. N^o. 184b § 3^b) keeps a finite value ²⁾, then from this should follow a finite difference for $S_{liq} - S_{sol}$ at $T=0$.

In order to get some opinion about the extent of such a possible difference of entropy we will put as final value at $T=0$ of $\frac{dp}{dT}$: 5 atm./ $^{\circ}$ K.

¹⁾ This last possibility has not been mentioned in Comm. N^o. 184b. Also Dr. VAN LAAR does not speak about it. I especially wish to establish the fact here that this possibility must indeed not be lost sight of.

²⁾ Should $v_{liq} - v_{sol}$ become $= 0$ at $T=0$, then also in this case S_{liq} should become $= S_{sol}$ at $T=0$.

almost agreeing with the inclination of the melting-curve between $1^{\circ}.2$ and $1^{\circ}.5$ K. As to $v_{liq} - v_{sol}$ it follows from the visual observations mentioned in Comm. N^o. 184b § 3^b, that this difference will only be a small fraction of for instance v_{liq} . If we put as utmost limit¹⁾ 5% then we get $v_{liq} - v_{sol} = 0,05 \times 7 \times 4 = 1,4$ cm³/mol. Then we should find $S_{liq} - S_{sol} = 7$ atm. cM³/° K. mol. = 0,18 cal./° K. mol. = 0,1 R.

This result, which is got with a value of $v_{liq} - v_{sol}$ which is very much greater than I think probable, is already one order of magnitude smaller than the differences of the zero point-entropies, which we find mentioned in literature as found or as probable²⁾.

The equation given by TAMMANN³⁾: $T-1 = \log(p-24)$, which he emphatically wished to have considered as interpolation-formula and only applicable to a small region of temperature, would give a very much smaller value of $\frac{dp}{dT}$ for $T=0$, and so together with the value accepted for $v_{liq} - v_{sol}$ mentioned above a very much smaller value of the difference of the zero point-entropies, to say for the latter 0,004 R.

Even if the heat-theorem of NERNST in its former formulization according to which the entropy of a material at $T=0$ had to be the same in all conditions, provided they are condensed, should not be strictly valuable, then this would yet be very near the case for helium solid and liquid.

As a matter of course however the question arises here whether it is not to be considered probable on statistical-theoretical grounds that we must understand this result in this way that the entropy-difference between solid and liquid helium at $T=0$ becomes strict 0 instead of approaching to a small fraction of R.

Though in my opinion an answer to this question cannot be given with surety at this moment⁴⁾ yet I think that this fact that a value of $S_{liq} - S_{sol}$ smaller (probably very much smaller) than 0,1 R does not answer to the expectation that in $S' - S'' = k \ln(Z'/Z'')^n$, the ratio Z'/Z'' of the probabilities of condition at $T=0$ can be expressed by a quotient of small whole numbers, gives cause to answer this question in the affirmative for the present.

§ 3. I might subjoin here still the following remarks⁵⁾.

1. I cannot perceive that Prof. PLANCK is guilty of a „thermodyna-

1) The small difference in refraction-index, which has to be accepted in order to explain that the surface of demarcation between solid and liquid was invisible, points to a very much smaller difference in density than was accepted here as highest limit.

2) F. SIMON, Handbuch d. Physik. X, p. 395, 1926. A. EUCKEN und F. FRIED, Zs. f. Phys. 29, 36, 1924. A. EUCKEN, MÜLLER-POUILLET's Lehrbuch der Physik, 11te Aufl. Bd. III, 1ste Hälfte, p. 649. W. SCHOTTKY, Physik. Zs. 22, 1, 1921; 23, 9, 448, 1922.

3) G. TAMMANN, Ann. d. Phys. (4) 82, 240, 1927.

4) See f.i. F. SIMON l.c., and Zs. f. Phys. 41, 806, 1927.

5) In this translation the remarks have not been inserted to which Dr. VAN LAAR does not resort in his answer, These Proceedings, p. 957.

mical sofism" as Dr. VAN LAAR says. From the theorem which Prof. PLANCK puts first: „Beim Nullpunkt der absoluten Temperatur besitzt die Entropie eines jeden chemisch homogenen festen oder flüssigen Körpers den Wert Null" follows necessarily $\left(\frac{\partial v}{\partial T}\right)_p = 0$ at $T = 0$.

Whether this is deduced from that by the more detailed reasoning of Prof. PLANCK or by saying: $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ and so it follows from $\left(\frac{\partial s}{\partial p}\right)_T = 0$ for $T = 0$, that it must then be $\left(\frac{\partial v}{\partial T}\right)_p = 0$, is of no consequence.

The reproach that this theorem to be proved is already implied in the theorem from which is started, is not fair: it cannot be wished that from the premises something is being deduced that is not implied.

2. Dr. VAN LAAR cannot know that the specific heat of liquid helium by¹⁾ constant volume remains finite at $T = 0$ (loc. cit. p. 247). The experiments of DANA and KAMERLINGH ONNES²⁾ which, however, don't go any further than 2° 5 K., would sooner give rise to expect that that specific heat does come up to 0.

Whether by liquids (and eventually by gases) at a sufficiently low temperature there appears a "degradation of energy" remains as yet an open question.

Wishing to derive from a presupposed opinion thereabout founded upon a very weak argumentation, that the energy in the liquid phase follows the T -law (VAN LAAR l.c. 247) is, to my opinion, not permitted.

If we follow the argumentation of Dr. VAN LAAR on p. 248 then it appears that the condition submitted by him that the $\frac{dp}{dT}$ for the melting-curve should become ∞ for $T = 0$ is only founded on this acknowledgement of the energy in the liquid phase.

While it appeared in § 2 that the direct experiments do not at all point to a course of the melting-curve at lower temperatures as is desired by Dr. VAN LAAR, we see here that this desire of Dr. VAN LAAR has no reasonable ground,

¹⁾ It has not become clear to me what signifies here the addition "(infinitely great)".

²⁾ L. I. DANA and H. KAMERLINGH ONNES, These Proceedings, 29, 1061, 1926. Comm. Leiden N^o. 179d.