

Citation:

H. Kamerlingh Onnes & W.H. Keesom, The vapour pressures of hydrogen from the boiling point down to near the triple point, in:

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has been explained by EINSTEIN and STERN in a satisfactory manner by the assumption of a zero-point energy.

2. The assumption of a zero-point energy for the translational motion of gas-molecules appears to be also required ¹⁾.

3. KEESOM ²⁾ has shown that the quanta-theory with the additional assumption of a zero-point energy is of great importance in the theory of free electrons in metals and removes a number of difficulties inherent in the equipartition-theory.

4. In conclusion it is shown in this paper, that the assumption of a zero-point energy for the rotations finds a strong support in the observations on the susceptibility of paramagnetic substances; it appears that by means of it the majority of the deviations from CURIE'S law observed at low temperatures ³⁾, which seem to be reducible to three seemingly largely different types may be correlated ⁴⁾ and quantitatively explained in a satisfactory manner.

Physics. — "*The vapour pressures of hydrogen from the boiling point down to near the triple-point.*" By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N^o. 137d (*On the measurement of very low temperatures. XXIII*) from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 28, 1913).

§ 1. The vapour pressures of hydrogen between the boiling point and the triple-point have been determined by DEWAR ⁵⁾ and by TRAVERS and JAQUEROD ⁶⁾. The value, which was obtained at

¹⁾ Communication to the Wolfskehl-Congress at Göttingen by H. KAMERLINGH ONNES and W. H. KEESOM. Comp. also W. H. KEESOM. Comm. Suppl. N^o. 30a.

²⁾ W. H. KEESOM. Comm. Suppl. N^o. 30b.

³⁾ The abnormal behaviour of anhydrous ferrous sulphate which has a maximum in its susceptibility is here left out of account.

⁴⁾ The theory given in this paper confirms the supposition by KAMERLINGH ONNES and PERRIER mentioned in § 1, that as regards paramagnetism corresponding temperatures exist, which must be taken proportional to a definite temperature, characteristic of each substance; on the above theory the temperature of maximum-susceptibility chosen by the authors for the purpose is to be replaced by the "internal" temperature $\frac{1}{2} \frac{h\nu_0}{k}$, which may be calculated from the zero-point energy.

⁵⁾ J. DEWAR. Proc. Roy. Soc. London, A. 76 (1905), p. 336.

⁶⁾ M. W. TRAVERS and A. JAQUEROD. Phil. Trans. (A) 200 (1902), p. 155.

Leiden for the heat of vaporization of hydrogen at the boiling point¹⁾, differed, however, appreciably from the values which follow with the aid of the CLAPEYRON-CLAUSIUS formula from the measurements of the vapour pressures mentioned above, taking into account the compressibility of hydrogen vapour according to the measurements of KAMERLINGH ONNES and W. J. DE HAAS²⁾. A deviation between the AVOGADRO scale of temperatures fixed by the aid of the gas thermometer, and the KELVIN scale of temperatures³⁾ of such an amount as would be indicated by the difference between these results may be considered improbable⁴⁾. It seemed therefore of interest to undertake a new determination of the vapour pressures of hydrogen in the region mentioned.

§ 2. The measurements were made with the aid of a vapour pressure apparatus as described by KAMERLINGH ONNES and BRAAK in Comm. No 107*a* (May 1908) Pl. I apparatus A.

The temperatures were measured⁵⁾ with the aid of the platinum resistance thermometer⁶⁾ Pt_r . We could avail ourselves of a more recent comparison (May 1913) of Pt_r with the hydrogen thermometer performed at 6 points, regularly distributed over the range from the boiling point to near the triple-point, by KAMERLINGH ONNES and HOLST in their research concerning the comparison of the scales of the hydrogen and the helium thermometers. The corrections⁷⁾ to

1) For a preliminary report see: W. H. KEESOM, *Handelingen 13de Nat. en Geneesk. Congr.* 1911, p. 181. According to a later calibration of the ampère- and voltmeter, which were used, with the aid of a water calorimeter the values given there are to be diminished by an amount of 2⁰/₁₀₀. Hence the value found with the smallest velocity of vaporization for the heat of vaporization of hydrogen at the boiling point (more accurately at an average pressure of 751,5 mm) becomes 110,2 cal₁₅. The vapour pressures according to DEWAR lead to the value 106, whereas those according to TRAVERS and JAQUEROD give a still smaller value.

2) H. KAMERLINGH ONNES and W. J. DE HAAS. *Comm.* N^o. 127*c* (May 1912).

3) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. *Math. Enz.* V 10, Leiden. *Comm. Suppl.* N^o. 23, § 82*a*.

4) This view is supported by the fact, that KEESOM, *Suppl.* N^o. 30*a* § 4, has found that the application of the quantum-theory with the introduction of the zero-point energy to the molecular translatory motion for a gas at such a density that the dimensions and the mutual attraction of the molecules need not to be considered, leads to an appreciable divergence from the equation $p = RT/v$ at extremely low temperatures only.

5) We gladly record our cordial thanks to Mr. G. HOLST for the aid afforded to us by performing these temperature measurements.

6) The bath was kept constant within 1/300 of a degree.

7) The corrections given here differ somewhat from those given in the Dutch edition of this paper, in accordance with the results of the research of KAMERLINGH ONNES and HOLST mentioned in the text.

the KELVIN scale for this hydrogen thermometer ($p_{000} = 120$ c.m.) (+ 0.14 down to -253° , + 0.15 for -254° and -255° , + 0.16 for -256° , + 0.17 for -257° , + 0.18 for -258° , + 0.20 for -259°) were deduced down to -257° from the corrections of the scale of the international hydrogen thermometer found for this region by KAMERLINGH ONNES and W. J. DE HAAS, Comm. No. 127c (June 1912), those for the lower temperatures were calculated according to the research of KAMERLINGH ONNES and HOLST mentioned above.

75.95 cm. of mercury was adopted as the international atmosphere¹⁾ at Leiden.

§ 3. The results are given in the following table.²⁾

Vapour pressures of hydrogen.						
θ KELVIN degrees	p internat. cm. of mercury	$p_{\text{calc.}}$	$p_{\text{obs.}} - p_{\text{calc.}}$	$\theta_{\text{obs.}} - \theta_{\text{calc.}}$	pressure of the bath	
-252.63	78.91	79.01 ⁵	- 0.10 ⁵	0.00	78.34	much liquid
[252.66	77.97	78.33	- 36	- 2]	78.15	" "
253.76	56.07	56.02	+ 5	0	55.62	" "
255.12	35.17	35.10	+ 7	+ 0 ⁵	35.26*	" "
255.17	34.53 ⁵	34.46	+ 7 ⁵	+ 0 ⁵	34.18	" "
256.08	24.16	24.20	- 4	0	24.00*	" "
256.08	24.19	24.20	- 1	0	24.47 ⁵ *	little "
256.09	23.99	24.11	- 12	- 1	23.77	much "
257.19	14.97	14.95	+ 2	0		" "
258.31	8.60	8.60	0	0	8.53	" "

The difference 0.03 cm. between the values of the pressure found at $-256^\circ.08$ with much and with little liquid corresponds to a difference in temperature of 0.003 of a degree and lies within the limits of accuracy; moreover it is in a direction opposite to that

¹⁾ Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. No. 23 Einheiten α .

²⁾ The numbers given in this table, and those derived from it further on in this paper differ slightly from those given in the Dutch edition in accordance with the slightly altered values of the corrections to the KELVIN scale (cf. 441 p. note 7) and an improved calculation of the temperatures.

which would follow from the supposition of an increase of pressure at condensation; hence there is no evidence of an influence of admixtures.

The pressure in the cryostat has also been given in the table (column 6). The manometer, on which this pressure was read, was connected to a side tube of the cover of the cryostat; this cover had at this place the same width as the cryostat glass. At the pressures marked with an * the tube, which formed the connection with the manometer, was continued within the cryostat by a glass tube which reached down into the liquid¹⁾. By this means we obtained the result that the vapour pressure was measured at a liquid surface where no continued vaporization (and hence cooling of the upper layers) takes place. The influence of this can be clearly seen: in the observations without * for all but one²⁾ the pressure of the bath was found smaller than that in the vapour pressure apparatus, for the observations with * just the reverse is the case. On the average in these latter observations the difference is moreover smaller. The temperature difference which corresponds to the largest pressure differences is 0.03 degrees. If for the measurement of the temperature in liquid hydrogen one is satisfied with this degree of accuracy, it is sufficient for the purpose to measure the pressure in the cryostat in the way indicated.

As the triple-point could not be properly observed in the vapour pressure apparatus, for determining the triple-point temperature the temperature of the bath was read when the first crystals became visible in the latter. The indication of P_{t_f} then became constant; 1.415 Ω was read. Extrapolation (over 0.8 degree) of the calibration curve of P_{t_f} gives for the triple-point temperature — 259° 14 C. in KELVIN degrees = 13° 95 K. The pressure of the bath was 5.07 cm. at this point.

§ 4. The curve which represents $\log p$ as a function of $\frac{1}{T}$ is slightly concave upwards.³⁾ In the 3rd column the values are given of p

¹⁾ In order to have a better guarantee that the pressure which is read belongs to the temperature of a definite place in the liquid, this tube might be surrounded by a heat conducting tube reaching above the liquid surface, as in the vapour pressure apparatus (cf. N^o. 107a, Pl. I).

²⁾ For this one, placed between [], the experimental data indicate that in the vapour pressure apparatus temperature equilibrium probably was not yet arrived at. [Added in the translation].

³⁾ The measurements of TRAVERS and JAQUEROD give a $\log p$, T^{-1} -curve which is slightly *convex* upwards. The following table gives some numbers which

calculated from a WREDE-RANKINE-KEESOM formula^{1) 2)}:

$$\log p = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2} \quad \dots \quad (1)$$

The 4th column gives the differences of the observed values and the values calculated from (1), the 5th column the corresponding differences in temperature.

From (1) follows for the boiling point: 20.33°K. = -252.76°C.³⁾

Extrapolation by (1) would give 5.41 cm. for the pressure corresponding to the triple-point temperature found in § 3 (with extrapolation of the calibration curve of P_{t_j}). The double extrapolation makes this value somewhat uncertain; it can in the mean time be regarded as a confirmation of the value found by KAMERLINGH ONNES and BRAAK⁴⁾.

§ 5. The heat of vaporization of hydrogen at a pressure of 75,15 cm. calculated according to CLAPEYRON-CLAUSIUS from (1), if for calculating v_{vap} the value $B_{A(71)}$ is taken from KAMERLINGH ONNES and W. J. DE HAAS, Comm. N^o. 127c, with v_{liq} after KAMERLINGH ONNES and CROMMELIN, Comm. N^o. 137a, becomes:

$$\lambda = 105.5 \text{ cal}_{16}.$$

enable a comparison with the data given by TRAVERS and JAQUEROD.

p internat. cm. of mercury	T KELVIN-scale (K.O. and K)	T^* KELVIN-scale (T. and J.)
76	20.33	20.33
35	17.96	17.90
10	15.07	15.07

*) Temperatures measured with a hydrogen thermometer, corrected by us to the KELVIN scale with corrections derived from the numbers given in § 2. [Added in the translation].

1) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N^o. 23, § 83 g.

2) Cf. 442 p. note 2.

3) This number coincides with that derived from the measurements of TRAVERS and JAQUEROD, cf. note 1. [Added in the translation].

4) H. KAMERLINGH ONNES and C. BRAAK. Comm. N^o. 95e (Oct. 1906). According to (1) to the pressure 5,38 cm. found there a temperature of 13° 94 K. corresponds.

This 'value¹⁾ is smaller than that found by direct measurement at the smallest velocity of vaporization²⁾: 110.2. It is possible that this result indicates that the precautions taken to prevent condensation of the vaporized hydrogen within the calorimeter have not been sufficient. In fact at a velocity of vaporization twice as great as that at which the value mentioned above was found smaller values were obtained, *viz.* 108.5 and 109.3 at 76.1 and 77.75 cm. pressure respectively.

Physics. — "*Vapour pressures at very low reduced temperatures.*

II. *The vapour pressure of carbon dioxide in the range from — 140° C. to about 160° C.*" By SOPHUS WEBER. Communication No. 137c from the Physical Laboratory at Leiden. (Communicated by Prof. KAMERLINGH ONNES).

(Communicated in the meeting of September 27, 1913).

§ 1. In these measurements the heated-wire manometer described before was used³⁾; it was calibrated by the aid of a set of pipettes as shown in fig. 1. The manometer is sealed to the vessel P_2 at J and is placed, together with P_1 and P_2 in a waterbath, in which a temperature of about 20° C. is maintained by means of a thermostat. This temperature is read on a mercury thermometer. The electric connections are the same as in fig. 4 of the first paper. In order to keep back mercury vapour or other vapours which might originate in P_2 the tube I the volume of which is only 1% of the whole volume was placed in alcohol cooled to about — 100° C. by the aid of liquid air. In a high vacuum the vapours given off by the grease of the stopcocks will be condensed in I . I have tried to prevent this flow of vapour to I while retaining the taps by interposing at

¹⁾ It may be noticed that this value nearly coincides with that calculated from the vapour pressure measurements of DEWAR (cf p. 441 note 1). The difference which shows the value derived from the vapour pressure measurements of TRAVERS and JAQUEROD (cf. p. 441 note 1) is due to the diverging course of their vapour pressure curve, cf. p. 444 note 1. [Added in the translation]

²⁾ Cf. p. 441 note 1.

³⁾ H. KAMERLINGH ONNES and SOPHUS WEBER, Comm. N^o. 137b (June 1913).