Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

by T_1 and T_2. First of all on account of the theoretical existence of *hidden* three-phase-pressure; but also because the presence or absence of a hidden plaitpoint does not coincide with the intersection or non-intersection of $\dfrac{d^2\psi}{dx^2} = 0$ and $\dfrac{d^2\psi}{dv^2} = 0$. Moreover the existence of the liquid state is also assumed here for all temperatures, however low. The occurrence of the solid state may, of course, be a hindrance for the observation of what we have called the temperature T_1. Thus in mixtures of water and phenol an upmost temperature limit has been found for three-phase-pressure; but it is still an open question whether there also exists a lowest temperature, higher than the absolute zero point.

(To be continued)

Physics. — *"On the measurement of very low temperatures. XXI. On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures."* By Dr. H. KAMER-LINGH ONNES and Dr. C. BRAAK. Communication N°. 107^a from the physical laboratory at Leiden.

(Communicated in the meeting of May 30, 1908).

§ 1. *Introduction.* In a preceding Communication N°. 101^a (Dec. '07) we have spoken of the desirability of determining once for all certain temperatures by means of boiling point apparatus, because the points of the temperature scale thus fixed have the advantage over those fixed with resistance thermometers and thermo-elements that they do not depend on the durability of special apparatus and they facilitate comparisons between thermometers in different laboratories.

This Communication treats of a number of determinations with oxygen: *a.* a little above and a little below the normal boiling point from which the latter could be derived; *b.* at 366 and 516 mm. mercury pressure which may serve to give information about the further course of the vapour pressure curve.

After some preliminary determinations we have constructed two apparatus. of different dimensions, in each of which different quantities of gas could be successively condensed. Thus we have obtained two series of independent determinations; at the same time the purity of the gas could be tested.

§ 2 *The measuring apparatus.* (See Pl. I).

In the vapour pressure apparatus of the small pattern A about 120 cc. gas can be condensed, in the large pattern B about 1 Liter. Pattern A consists of a bulb a of 0.5 cc. with a glass stem b, connected to a manometer with a steel capillary c. The manometer consists of two tubes $m_1 m_2$ of 2 cm. bore filled with mercury; they are connected by an india rubber tube. An air-trap d prevents impurities from coming into the gas. The glass stem is moreover surrounded by a copper cylinder e and a glass jacket f by means of which heat is conducted from above, thus preventing the temperature at any part of the apparatus from falling below that of the bulb which is placed in the cryostat at the place where the temperature is measured. By pressing the mercury higher up or lower down one can condense different quantities of gas successively.

The construction of pattern B differs a little from that of A; this is especially in order to avoid the apparatus becoming difficult to handle because a too large quantity of mercury would be required. The manometer $m_1 m_2$ consists of a U-tube of glass of which the two limbs are separated by a glass cock k_1. This U-tube is blown on to another $d_1 d_2$ which contains the gas. The two limbs of the latter are cylinders of 70 c.m. length and 0.5 liter contents separated by a cock k_2. The limb d_1 connected to the manometer is fixed at its upper end to the steel capillary c which is connected with the bulb a. The limb d_2 carries a glass cock k_3, through which the apparatus is filled. The reservoir is filled to 1 atm. excess of pressure with gas. By first shutting k_3 and then opening it we can condense first the gas of d_1 which is under an excess of pressure, then also that of d_2.

A enables us to judge of the purity of the gas when we investigate in how far the vapour pressure measured depends on the fraction of the quantity of gas already condensed. By means of B, where the quantity of condensed gas always amounts to the same portion of the total quantity, we can determine in how far the vapour pressure is independent of the increase or decrease of the quantity of the condensed gas itself.

The oxygen is prepared from potassium permanganate through heating. After it has been carefully purified and dried over a KOH-solution and P_2O_5 the gas is condensed in a bulb immersed in liquid air. Then the liquid air is removed and the apparatus are filled with the evaporated gas.

The pressure was read with a cathetometer; this does not require a very high degree of accuracy because of the great variability of

the vapour pressure with the temperature. The atmospheric pressure on the mercury in the open manometer was read on an aneroid barometer which we occasionally compared with a mercury barometer.

§ 3. *The determination of temperature and the degree of accuracy*.

For measuring the temperature we have used for the determinations in the neighbourhood of the boiling point of oxygen the resistance thermometer Pt'_1, which has been compared [1] (comp. Comms. N°. 95c Sept. '06 and N°. 101a Dec. '07) over a large range with the hydrogen thermometer of Comm. N°. 95r (Oct. '06) which we shall call B_{III}; for — 182° this was done on March 25th 1907 (comp. Comm. N°. 101a table I). Some calibrations have afterwards been made, which together with those just named are given in table II. This table also contains the results of an indirect comparison of Pt'_I with another hydrogen thermometer, which we call T_4 and which was used in an investigation of Dr. FEUSTEL and one of us (K. O.) with a differential thermometer helium-hydrogen, which investigation will soon be published.

In connection with § 4 of Comm. N°. 101a we have also given in table I the results of 4 comparisons between two resistance thermometers Pt'_1 and Pt''_d[3]) at about — 183° C. and — 217° C.

TABLE I. Comparison between Pt'_1 and Pt'_d.			
Date	Pt'_1	Pt''_d	Pt'_1 and Pt'_d in degrees
22 June '07	34.267	18.565 [2])	0°.000
18 Dec '07	34.359	18.609	
24 June '07	14.761	9.1483 [3])	0°.007
19 Dec. '07	14.824	9.1793	

For the measurements on 18th and 19th Dec. '07 B_{III}, Pt'_1 and

[1]) $W_{Pt1} = 1.01806\ W_{Pt1}$ (comp. § 2 of Comm. N°. 101a Dec. 1907).

[2]) This resistance thermometer is the same as the one which in Comm. N°. 99b (Sept. '07) is called Pt'_d. Afterwards it has broken in the middle, and consequently the resistance was diminished to half its value (Pt'_d). Here it is indicated with two accents because it has then undergone a small reparation owing to which $Pt''_d = 1.00073\ Pt'_d$ at 0°.

[3]) This value has been reduced with the factor of the preceding footnote.

Pt''_d were placed in the cryostat. Thus we simultaneously obtained the results relating to them of the tables I and II. Those of the second part of table II are derived from a comparison between Pt''_d and T_4. The resistances observed were reduced with the factor 1.00073 (cf. the footnote on the preceding page), giving 18.560 and 18.398 Ω. These have been reduced with the data of table I to Pt'_1. This yields the values of the third column.

The calibration of T_4 agrees satisfactorily with that of B_{III}. The mean of the deviations for the two former and the two latter data differs from table II by 0.022 Ω which corresponds to 0°.038. This small difference between the readings of two entirely different gas thermometers satisfactorily confirms the exactness of the limit of accuracy derived formerly (Comm. N°. 95ᵉ) and enhances the reliability of the other preceding determinations of temperature.

TABLE II. Comparison of the resistance thermometer Pt'_I with the hydrogen thermometers B_{III} and T_4.

	Comparison with B_{III}		
Date	Temperature according to the hydrogen thermom. B_{III}	Resistance in Ω	$^OPt'_I - ^CA_I$
25 March '07	— 182°.352	34.492	— 0 008
18 Dec. '07	— 182°.595	34.359	— 0.000
17 Febr. '08	— 186°.599	32 027	— 0.019
18 Febr. '08	— 189°.50)	30 332	— 0.041
19 Dec. '07	— 216°.840	14.824	+ 0 031
	Comparison with T_4		
30 Nov. '07	— 182°.736 [1])	34.257	— 0.021
3 Dec. '07	— 183°.302 [1])	23.919	— 0.031

[1]) The hydrogen thermometer temperatures are calculated on the scale of Comm. N°. 95ᵉ (Oct. '06). As the zero pressure amounted to about 1360 mm. we have accordingly accepted for the coefficient of pressure variation 0.0036629, derived from the coefficient of pressure variation of Comm. N°. 60 (Sept. 1900) (0.0036627 for 1100 mm. zero pressure). We have also applied a correction according to the difference of the correction to the absolute scale for 1360 and 1100 mm. zero pressure.

The tables I and II also give new data about the accuracy of the readings of the resistance and of the gas thermometer[1]). According to table I the error of the resistance remains below $0.°01$. As to the readings of the gas thermometer, the first two data of table II inter se yield a difference smaller than $0.°02$. With the difference $+ 0.031 \, \Omega$ at $— 217°$ correspond $+ 0,028$ and $+ 0.016$ of table II in Comm. $N°. 95^e$ and table I in Comm. $N°. 101^a$. This also agrees with the accuracy of $0.°02$ derived in § 7 of Comm. $N°. 95^e$. This seems not to be the case. for the value of 18 Febr. '08 which deviates rather much from the formula. It will depend on later determinations what part of this deviation must be ascribed to the formula AI.

§ 4. *The vapour pressure determinations in the neighbourhood of the boiling point of oxygen.*

We have used the cryostat described in Comm. $N°. 94^f$ (Pl. V) Sept. 1906). The temperature was determined and regulated with the resistance Pt'_1 placed in the bath. The deviations of the galvanometer were so small that no correction was required for it. In the apparatus A the mercury was raised successively in the lower and the upper end of the manometer m_1, in B first the gas of one reservoir was condensed, afterwards of the two reservoirs. This is indicated in the following table with "little" and "much". Table III contains a determination at a small excess of pressure, another at a pressure of a little below 760 m.m. and a determination for control also at an excess of pressure. The pressure is reduced to $0°$ C. The last column contains the deviations from the mean for each series.

The resistances of the thermometer read on the WHEATSTONE bridge were for the three series respectively:

$$34.433 \quad , \quad 34.098 \quad \text{and} \quad 34.433 \, \Omega.$$

If we compare the results obtained with the condensation of a little quantity of gas with those with the condensation of a large quantity we cannot find any systematical deviations, which speaks for the purity of the gas used. In case impurities should occur their influence on the vapour pressure derived with the smaller condensation is sure to be less than the influence on the difference just mentioned. It may therefore, be neglected.

---

[1]) Comp. Comms. No. 95^c, 95^e and 101^a.

Date	Time			Pressure in m.m. mercury	Mean of a series	Deviation from the mean
TABLE III Vapour pressure of oxygen in the neighbourhood of the boiling point.						
	h					
6 Febr. '08	4 31'	large pattern (little)		806.34		—0.37
excess of pressure	4 46	small ,, (much)		806.55	806.71	—0.16
Series I	5 0	,, ,, (little)		806 98		+0 27
	5 8	large ,, (much)		806.97		+0.26
7 Febr. '08	10 13	small ,, (little)		759 47		− 0 14
pressure a little below 760 mm.	10 21	,, ,, ,,		759.75		+0.14
Series II	10 50	,, ,, (much)		759.46		—0 15
				759 54		—0.07
	11 12	large ,, ,,		759.35	759.61	—0 26
				759 51		—0 10
	11 47	,, ,, ,,		759 76		+0.15
	12 26	small ,, (little)		759.84		+0.23
	12 37	large ,, (much)		759.82		+0.21
7 Febr. '08	1 20	small ,, (little)		806.17		—0 09
excess of pressure	1 25	large ,, (much)		806.30	806.26	+0.04
Series III	1 35	small ,, (little)		806 31		+0.05

§ 5 *Accuracy of the adjustments*.

From the results of table III we derive the following data.

The deviations from the mean which must be ascribed partly to the regulation of the temperature are small and when reduced to differences of temperature they remain below $0°.005$.

The mean of the results of the large and the small pattern derived separately for each series gives:

    Series   I, large pattern $p = 806.65$ (2 observations)
                  small   ,,   806.76 (2   ,,   )
    Series II, large   ,, $p = 759.64$ (5   ,,   )
                  small   ,,   759.58 (4   ,,   )
    Series III, large   ,, $p = 806.30$ (1 observation)
                  small   ,,   806.24 (2 observations)

The difference between the two means is at the utmost 0.1 mm. which corresponds to $\dfrac{1°}{800}$. Thence we may conclude that a vapour pressure apparatus is extremely suited for the standardizing of temperatures. The data obtained here show that in this respect the apparatus surpasses the gas thermometer and probably also the resistance thermometer. For the hydrogen thermometer, namely, the error of 2 adjustments amounts to 0 .01 à $0°.02$ (comp. § 3 and Comm. N°. 95^c § 8 and N°. 101^a § 3), for the resistance thermometer to $0°.01$ (comp. § 3 and Comm. N°. 101^a § 4) [1]).

§ 6. *The determination of the boiling point of oxygen.*

With the resistances of Pt'_1 given in § 4 we can by means of the data of table II derive the corresponding temperatures on the scale of our hydrogen thermometer B_{III}. To this end we start from the mean of the two data of March 25 and Dec. 18, '07, because these are probably more accurate than those obtained with the thermometer T'_4. To 34.433 and $34.098\,\Omega$ correspond the temperatures $-182°.460$ and $-183°.040$ respectively. To the first. belongs the vapour pressure 806.40 m.m. (the mean from the series I and III) to the second 759.61 mm. (series II). Thence follows by means of rectilinear interpolation for 760 mm. at Leiden for the temperature on the thermometer B_{III} : $t = -183°.035$ and for the normal boiling point (760 mm. on sea-level and 45° northern latitude):

$$t = -183°.030 - 0°.007 = -183°.037$$

on the normal hydrogen thermometer and (comp. table XXV of Comm. N°. 101^b Dec. 1907)

$$\theta = -183°.042 + 0°.056 = -182°.986$$

on the absolute scale.

If we take into consideration the degree of accuracy of the correction to the absolute scale (comp. Comm. N°. 97^b March '07) and the results for the control determinations for the measurement of temperature made as well with the same hydrogen thermometer as with different ones, then it follows that this value does not probably deviate from the real value by more than $0°.03$.

---

[1]) The data of table III also enable us to judge of the accuracy of the adjustment of the resistance. Let the error in the reading of vapour pressure apparatus $= 0$, which approximately is permissible according to what precedes, then the difference of the means for the series I and III must be ascribed to the error of the measurement of the resistance. This then would be $0°.005$.

§ 7. *Vapour pressure determination at lower temperatures.*

For these measurements (comp. § 2 table II) the temperature was directly read on the hydrogen thermometer B_{III}; Pt'_I was used for the regulation. The temperatures are — $186°.599$ and — $189°.500$ (comp. table II). At the same time we obtained a new calibration for Pt_I. The determinations were made with only the small vapour pressure apparatus. The results are combined in table IV in the same way as in table III.

In the determinations marked (*a*) about half of the gas was condensed, in those marked (*b*) about $\dfrac{4}{5}$ of the gas. As was the case for the boiling point no systematic difference resulting from this seems to be perceptible. If we reduce the temperatures to the absolute scale and the pressures to sea-level and 45° northern latitude we find for:

$$\theta = -186°.542 \qquad p = 516.19 \text{ mm.}$$
$$\theta = -189°.442 \qquad p = 366.24 \text{ mm.}$$

TABLE IV. Vapour pressure of oxygen below the boiling point.

| Date	Time	Pressure in mm.	Mean of a series	Deviation from the mean
17 Febr. '08 (*a*)	2 55'ʰ	366.06	.	+0.07
(*a*)	3 30	365.90	365.99	—0.09
(*b*)	4 5	366.00		+0.01
(*b*)	4 25	365.98		—0.01
18 Febr. '08 (*a*)	10 42	515 82		—0.01
(*a*)	11 0	515 89	515.83	+0.06
(*b*)	11 30	515 69		—0.14
(*b*)	11 40	515.94		+0 11

§ 8. *The results compared with those of other observers.*

Of previous determinations those by TRAVERS, SENTER and JAQUEROD[1]) deserve most confidence, especially because these observers used pure oxygen in a closed reservoir. This is not the case with

---

[1]) Phil. Trans. Roy. Soc. Series A. Vol. 200. 1902

H. KAMERLINGH ONNES and **C. BRAAK.** "On the measurement of very
low temperatures XXI. On the standardizing of temperatures by means
of boiling points of pure substances. The determination of the vapour
pressure of oxygen at three temperatures."
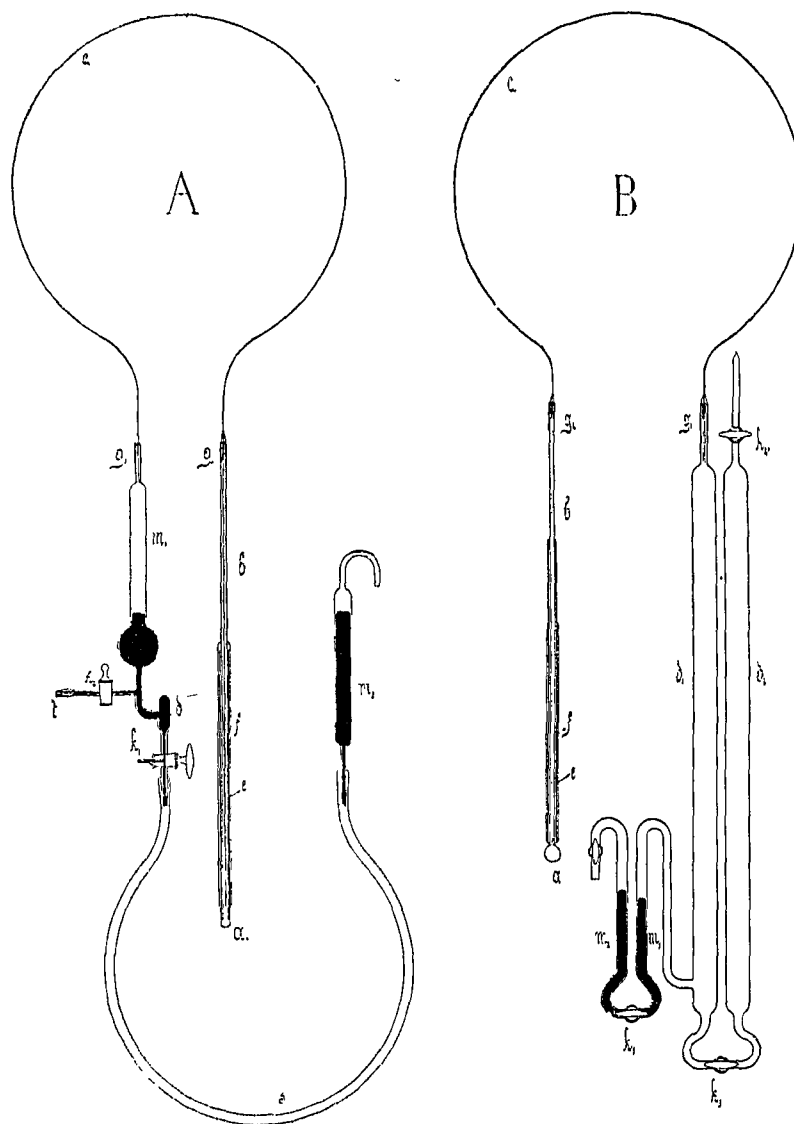
the other observations where the temperature of a bath of oxygen boiling under atmospheric pressure was determined. For then impurities, nitrogen as well as less volatile substances are unavoidable. It seems that the influence of the latter is paramount; all these results for the boiling point are too high by 0°.3 or more. The first mentioned determinations yield for the boiling point of oxygen —182°.93 on the normal hydrogen scale. For the pressure 760 mm. is given without indication of a further reduction. Our value for 760 mm. mercury (at 0°) is on the normal hydrogen scale —183°.030, differing by 0°.10 from the value mentioned above. One of the last determinations is that of Grunmach[1]. He finds —182°.23. With the correction derived by Hoffmann and Rothe[2] for the pentane thermometer (— 0°.42) this becomes —182°.66, a result which after being corrected is still much too high.

If we compare the two observations at lower pressure with those of Travers, Senter and Jaquerod then it appears that both our temperatures are lower by 0°.13. Hence it is clear that a systematic difference exists between the two series.

[1] Berliner Sitz. Ber. 1906.
[2] Zeitschr. f. Instrkd. 27. 1807.

(November 26, 1908).