## Physics. — New determination of the normal boiling point of oxygen. By W. H. KEESOM, Miss H. VAN DER HORST and Miss A. F. J. JANSEN. (Comm. N<sup>0</sup>. 203b from the Physical Laboratory at Leiden.)

(Communicated at the meeting of November 30, 1929).

§ 1. Introduction. Already on two occasions the normal boiling point has been determined at Leiden, namely by KAMERLINGH ONNES and BRAAK  $^{1}$ ) in 1908 and by CATH  $^{2}$ ) in 1918.

The results of these measurements do not agree exactly with each other. KAMERLINGH ONNES and BRAAK give a value of  $-182.98^{6\circ}$  C. (Celsius-Avogadro scale). If however in accordance with a remark of CATH <sup>3</sup>), we accept 0.0036628 for the pressure coefficient of the hydrogen thermometer with icepoint pressure 1100 mm we obtain for the normal boiling point,  $-182.98^{1\circ}$  C. If a further correction is applied, — so that the result represents the indications of the hydrogen thermometer when using the value of the thermal expansion of glass, given by VAN AGT and KAMERLINGH ONNES <sup>4</sup>) — this temperature comes to  $-182.97^{0\circ}$  C. This temperature refers to the Celsius-Avogadro scale, which is derived from the scale of the normal hydrogen thermometer, on the basis of  $a_{nH_2} = 0.0036627$ , by applying to it the corrections calculated by KAMERLINGH ONNES and BRAAK <sup>5</sup>).

CATH gives  $-182.95^{\circ}$  C. When calculated with the value of the expansion of glass given by VAN AGT and KAMERLINGH ONNES, it comes to  $-182.93^{9\circ}$  C. For the calculation of this temperature 0.0036614 was taken for the fundamental pressure coefficient of the helium thermometer with an ice-point pressure 1000 mm. If instead we accept for it 0.0036611, the value given by KEESOM and Miss VAN DER HORST <sup>6</sup>), the temperature becomes  $-192.95^{4\circ}$  C. This temperature refers to the Celsius-Avogadro scale, derived from the normal helium thermometer, on the basis of  $a_{nHe} = 0.0036611$  by applying to it the correction <sup>7</sup>) calculated by KAMERLINGH ONNES<sup>8</sup>).

<sup>2</sup>) These Proceedings 21, 656, 1918, Comm. Leiden N<sup>0</sup>. 152d.

<sup>8</sup>) Probably CATH has derived this correction from the column  $(\Delta t)_b$  of table I of Comm. N<sup>0</sup>. 102b. If this really is the case, then the value mentioned in the text must be further increased by + 0.014 (thus giving  $-182.94^{0\circ}$  C.) in order to be comparable with the value obtained in this communication, for which the correction is derived from the table given by CATH and KAMERLINGH ONNES, Comm. N<sup>0</sup>. 156a (also given in Suppl. N<sup>0</sup>. 51a table Xa).

<sup>1)</sup> These Proceedings 11, 333, 1908, Comm. Leiden N<sup>0</sup>. 107a.

<sup>3)</sup> Comm. Leiden N<sup>0</sup>. 152d, p. 48, note 1.

<sup>&</sup>lt;sup>4</sup>) These Proceedings 28, 667, 1925, Comm. Leiden N<sup>0</sup>. 176a.

<sup>5)</sup> These Proceedings 10, 429, 1907, Comm. Leiden N<sup>0</sup>. 101b.

<sup>6)</sup> These Proceedings 30, 970, 1927, Comm. Leiden N<sup>0</sup>. 188a.

<sup>7)</sup> These Proceedings 10, 589, 1907, Comm. Leiden N<sup>0</sup>. 102b.

Also at Berlin the boiling point of oxygen has been determined twice, namely by HENNING<sup>1</sup>) in 1914 and by HENNING and HEUSE<sup>2</sup>) in 1924. HENNING obtained a value of  $-182.97^{\circ}$  C., HENNING and HEUSE  $-183.00^{\circ}$  C. The measurements of 1914 are founded on observations by means of the hydrogen thermometer, the measurements of 1924 on observations by means of the helium thermometer. In both cases the authors corrected to the thermodynamic scale.

We decided to make a new determination of this boiling point, because the two values, obtained in Leiden, do not agree satisfactorily, and there is also a marked difference between those values and the latest value obtained in Berlin. Also the normal boiling point of oxygen is of great importance for the problem of fixing an international temperature scale <sup>3</sup>).

The matter was all the more important since we now could use for the measurements the same helium thermometer, as was employed for determining the fundamental pressure coefficient 4).

The measurements were made in 1927. For the final decision of the results, however, we have waited for the further investigation of the thermal expansion of Jena glass 16 III <sup>5</sup>). As to the expansion between  $0^{\circ}$  and  $100^{\circ}$  C. that investigation has cleared up only a small part of the difference between the results, obtained by VAN AGT and KAMERLINGH ONNES <sup>6</sup>), by measuring the linear coefficient, and those obtained by one of us <sup>7</sup>) by the method of the weight thermometer. Nevertheless the value of the expansion between —183° C. and 0° C. obtained by VAN AGT and KAMERLINGH ONNES has been found to be exact. So we consider that for this investigation we can use with confidence this value of the expansion of glass <sup>8</sup>).

§ 2. For these measurements there were suspended in a bath of liquid oxygen, that was stirred by means of a mechanical valve stirrer : a vapour pressure apparatus 9), filled with pure oxygen; the helium thermometer  $T_3$  with reservoir of 108 cm<sup>3</sup> (see Comm. N<sup>0</sup>. 188a, § 2); besides three

<sup>1)</sup> F. HENNING, Ann. d. Phys. (4) 43, 282, 1914.

<sup>2)</sup> F. HENNING und W. HEUSE, Zs. f. Phys. 23, 105, 1924.

<sup>&</sup>lt;sup>3</sup>) Comp. for this a communication of one of us, Comm. Leiden, Suppl. N<sup>0</sup>. 67b, which will soon appear in "Physica".

<sup>&</sup>lt;sup>4</sup>) W. H. KEESOM and Miss H. VAN DER HORST, These Proceedings **30**, 970, 1927, Comm. Leiden, N<sup>0</sup>, 188a.

<sup>&</sup>lt;sup>5</sup>) W. H. KEESOM and A. BIJL, These Proceedings, **32**, 1164, 1929; Comm. Leiden, N<sup>0</sup>. 203a.

<sup>6)</sup> These Proceedings 28, 667, 1925, Comm. Leiden N<sup>0</sup>. 176a.

<sup>7)</sup> These Proceedings 30, 970, 1927, Comm. Leiden N<sup>0</sup>. 188a, p. 5.

<sup>&</sup>lt;sup>8</sup>) If we suppose that the uncertainty in the expansion of glass between  $-183^{\circ}$  C. and  $0^{\circ}$  C. is proportional to the difference between the values for the expansion between  $0^{\circ}$  C. and  $100^{\circ}$  C., obtained by the two methods mentioned, this would cause an uncertainty of 0.006 degrees in the boiling point of oxygen.

<sup>9)</sup> See Comm. Leiden N<sup>0</sup>. 152d, p. 46.

platinum thermometers, of which one served for fixing and maintaining the temperature.

For the fundamental pressure coefficient of helium we used the value 0.0036611, obtained in Comm. N<sup>0</sup>. 188a. For the expansion of glass between  $-183^{\circ}$  C. and 0° C. we used the value, obtained by KEESOM and BIJL, which nearly agrees with the value of VAN AGT and KAMERLINGH ONNES. The correction to the Celsius-Avogadro scale was derived from Comm. N<sup>0</sup>. 156a, table V (conform to Suppl. N<sup>0</sup>. 51a table Xa).

The oxygen was prepared, by the method usual at Leiden 1), by heating  $KMnO_4$ .

§ 3. Results. The results of the measurements are given in table I.

Vapour pressures of oxygen			
Date	Temperature 0° C.	Pressure mm Hg at normal gravity	0—C degrees C
17 Nov. 1927	-182.628	789.234	+ 0.004
	—182.953	762.122	0
		744.033	+ 7
18 Nov. 1929		68 <b>4.2</b> 38	+ 10
	—183.515	719.569	- 12
и п п	—182.957	761.731	0

TABLE I

These results can be represented by the formula, derived by means of least squares :

 $t = -182.977 + 0.01231 (p - 760) - 0.00001624 (p - 760)^2$ , where p is given in mm. The column 0 - C gives the difference between observed and calculated temperatures.

§ 4. Hence the three determinations, performed at Leiden, gave the following values :

KAMERLINGH ONNES and BRAAK	—182.97°° C.
Сатн	—182.954 <i>,</i> ,
K., v. D. H. and J.	—182.97 <sup>7</sup> ,,

1) Comm. Leiden No. 117, p. 46 and H. A. KUYPERS, Diss. Leiden, 1924.

Owing to the uncertainty of the reduction of the two former determinations to the temperature scale now employed, the present result was given a "weight" 2 in obtaining the average. Whence the mean normal boiling point comes to

 $-182.97^{\circ} \pm 0.010^{\circ}$  C.

We conclude further, that the normal boiling point of oxygen can be reproduced with a mean error of  $\pm$  0.01 degree, and that it is suitable as a basic point on the temperature scale to that degree of accuracy.