Physics. — The melting-curve of hydrogen to 450 kg/cm<sup>2</sup>. By W. H. KEESOM and J. H. C. LISMAN. (Communication N<sup>0</sup>. 213e from the Physical Laboratory at Leiden).

(Communicated at the meeting of May 30, 1931.)

- $\S$  1. Introduction. The melting-curve of hydrogen was already investigated in this laboratory to 245 kg/cm²¹). There was a slight uncertainty in the manometer corrections of the last measurements, and therefore the whole curve was measured again and extended to 450 kg/cm². The method is the same as described in Comm. Nº. 184a.
- § 2. Apparatus. Pressures above 250 kg/cm<sup>2</sup> correspond to temperatures above the normal boiling-point of hydrogen; therefore a cryostat has been contructed <sup>2</sup>), in which the hydrogen boils under a pressure higher than 1 atm. (maximum 4 atm. above atmospheric pressure) and by means of which measurements can be made at temperatures between 20.3 and 27.5° K.

The temperatures below 20.6° K were measured with the platinum thermometer Pt 31; for higher temperatures Pt 64 was used, which has been calibrated between 20.3 and 27.3° K against Pt 24, the latter having been compared with the helium thermometer in 1926.

The pressures were read on a metal manometer, whose corrections were determined with a pressure-balance; these corrections were determined before and after the measurements. The pressure-balance has been compared with the pressure-balance of the VAN DER WAALS-foundation at Amsterdam; we are greatly indebted to Dr. A. MICHELS, who kindly allowed us to make this comparison in his laboratory. From this comparison the functional section of the two pistons P 1000 and P 250 of the Leiden pressure balance could be calculated. For pressures lower than 50 atm. the apparatus has been compared with the closed manometer M 60  $^3$ ), and the functional section of the pistons P 250 and P 60 was so determined.

The results are given in table I, which shows a good agreement between the Amsterdam and Leiden pressure-measuring.

<sup>1)</sup> H. KAMERLINGH ONNES and W. VAN GULIK, These Proceedings 29, 1184, 1926. Comm. Leiden №. 184a. W. VAN GULIK and W. H. KEESOM, These Proceedings 31, 1059, 1928, Comm. Leiden №. 192b.

<sup>&</sup>lt;sup>2</sup>) W. H. KEESOM and J. H. C. LISMAN, These Proceedings 34, 602, 1931, Comm. Leiden No. 213 f.

<sup>&</sup>lt;sup>3)</sup> Cf. C. A. CROMMELIN and MISS E. I. SMID, These Proceedings 18, 472, 1915. Comm. Leiden No. 146 c.

TABLE 1.

Functional section in cm. <sup>2</sup>	Calibration
0.2504 1)	Amsterdam
1.0002	Amsterdam
1.0002 ¹)	Leiden
4.0015 <sup>1</sup> )	Leiden
	in cm. <sup>2</sup> 0.2504 <sup>1</sup> ) 1.0002 1.0002 <sup>1</sup> )

§ 3. The results are given in table II and represented in Fig. 1; the differences with the earlier measurements are small. The slope of the curve

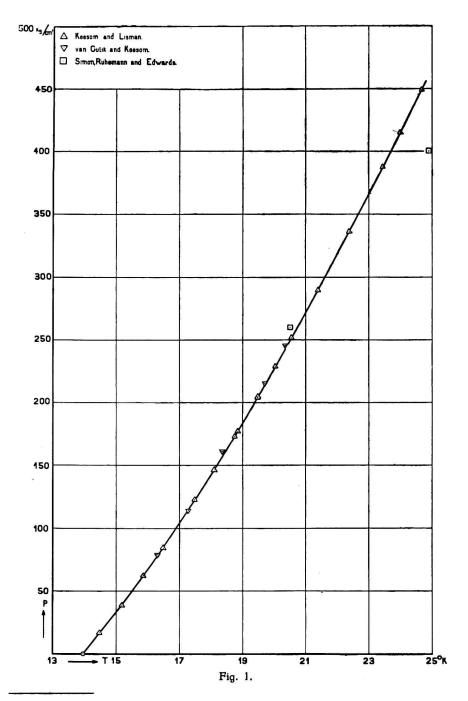
TABLE II.

T °K	p observed kg/cm <sup>2</sup>	p calculated kg/cm²	p <sub>obs.</sub> —p <sub>cale.</sub> kg/cm <sup>2</sup>
13.95 ²)	0.1	-1.35	1,45
14.47	16.5	15.5	1.0
15.18	38.9	39.5	-0.6
15.85	62.1	62.8	_0.7
16.48	84.7	85.6	-0.9
17.47	122.8	123.0	-0.2
18.10	146.2	147.7	<b>—1.5</b>
18.75	172.9	174.0	-1.1
18.87	177.1	178.9 <sup>5</sup>	-1.8 <sup>5</sup>
19.47	203.8	204.05	_0.2 <sup>5</sup>
19.48	204.5	204.5	o
20.03	228.8	228.1	0.7
20.54	251.7	250. <del>4</del> 5	1.25
21.385	289.9	288.6	1.3
22.38	336.2	335.2	1.0
23.43	387.6	386.3	1.3
24.01	414.9	415.35	_0. <b>4</b> 5
24.665	449.4	451.1	-1.7

<sup>1)</sup> The mean of the very little differing values at different pressures.

<sup>&</sup>lt;sup>2)</sup> Triple-point: H. KAMERLINGH ONNES and W. H. KEESOM, These Proceedings 16, 440, 1913, Comm. Leiden N<sup>0</sup>. 137 d.

is a little steeper than that of SIMON, RUHEMANN and EDWARDS' curve 1); whether this difference is caused by a different amount of para-hydrogen in the hydrogen used, must be left to further research.



<sup>1)</sup> F. SIMON, M. RUHEMANN und W. A. M. EDWARDS, Zs. f. phys. Chem. B. 6, 331, 1930.

The two points of SIMON and his coworkers, drawn in our figure, don't agree very well with our curve; it is to be considered indeed, that the relative accuracy of SIMON, RUHEMANN and EDWARDS' measurements was smaller at these pressures than at higher ones 1).

## § 4. We have tested whether SIMON and GLATZEL's formula 2)

$$^{10}log(a+p)=c^{10}log T+b$$
,

where a, b and c are constants, can represent our results.

We found with the method of least squares:

$$a = 242.3,$$
 $b = 0.26534,$ 
 $c = 1.84923.$ 

We calculated the pressures (third column of table II) and determined the differences between the observed and the calculated values of p (fourth column).

The deviations are systematical; so the formula can only be used as an interpolation formula, in combination with a deviation-curve.

Finally we calculated the meltingpressures corresponding to integer values of T (Table III).

TABLE III.

T °K.	p kg/cm²	p atm.
14	1.7	1.6
15	33.2	32.1
16	67.3	65.1
17	103.6	100.2
18	142.2	137.6
19	183.1	177.1
20	227.6	220.2
21	272.4	263.5
22	318.6	308.2
23	366.1	354.2
24	414.5	401.0
25	464.2	<b>44</b> 9.1

<sup>1)</sup> F. SIMON, M. RUHEMANN und W. A. M. EDWARDS, l. c. p. 337.

<sup>2)</sup> F. SIMON und G. GLATZEL, Zs. f. anorg. u. allgem. Chemie, 178, 309. 1929.