

**Physics.** — „On the Maximum and Minimum Density and the Heat of Evaporation of Helium.” (Second Part). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of October 30, 1926).

## B. Experimental Part.

### 1. The equation of the vapour pressure.

The experimental material is here, indeed, not very large, but still sufficient to derive a fairly reliable vapour pressure equation from it. In the following table the vapour pressures measured are given, and by the side of them the values of  $p$  calculated from the two formulae:

$$\left. \begin{aligned} \log^{10} p^{mm} &= -\frac{3,8308}{T} + 2,9044 + 0,2107 T \quad (0^\circ \text{ to } 4^\circ, 2) \\ \log^{10} p^{mm} &= -\frac{4,9874}{T} + 3,5083 + 0,1325 T \quad (3^\circ, 5-5^\circ, 2) \end{aligned} \right\} \dots (10)$$

The observations marked with an asterisk (bold type) are considered as the most accurate by the authors<sup>1)</sup>. For this reason they have been used for the calculation of the constants in both formulae. When the

TABLE I.

$T$	$p_{exp.}^{mm}$	$p_{form.}$	$T$	$p_{exp.}^{mm}$	$p_{form.}$
1.35	(3)	2.25	<b>*3.516</b>	359.5	359.5
<b>*1.475</b>	<b>4.15</b>	4.15	3.89	565	552
2.24	51	46.4	<b>*4.205</b>	<b>757.5</b>	757.5
3.17	(197)	231	4.21	760 } 767 }	761
<b>*3.516</b>	<b>359.5</b>	359.5	4.90	(1329)	1380
3.89	565	549	5.04	1520	1536
<b>*4.205</b>	<b>757.5</b>	757.5	5.09	1569	1596
4.21	760 } 767 }	761	5.16	1668	1681
			<b>*5.19</b>	<b>1718</b>	1718

<sup>1)</sup> K. ONNES, Comm. 119<sup>a</sup> (1911) and 124<sup>b</sup> (1911); K. ONNES and S. WEBER, Comm. 147<sup>b</sup> (1915).

experimental values are represented grafically ( $T \log p$  against  $T$ ), it is at once perceived that the pressures at  $1^{\circ},35$ ,  $3^{\circ},17$  and  $4^{\circ},90$  (placed between brackets by us) are *not* in conformity with the others (one too high, the two others too low), and can, therefore, be left out of consideration in the calculation of the formulae. If this is overlooked, it leads of course to great disappointment, and the method of least squares will be of no use; which method is mathematical nonsense with a comparatively small number of observations. In contrast with the said values, those at  $2^{\circ},24$ ,  $3^{\circ},89$ ,  $5^{\circ},04$  and  $5^{\circ},16$  are in pretty good harmony with the others.

The coefficient 4,9874 in our second formula, of course, lacks the physical meaning of the corresponding coefficient 3,8303 in the first formula, viz.  $= \lambda_0 : R$ , because the second formula is only valid to  $3^{\circ},5$  downwards.

The onlogically built formula of Comm. 147*b*, where the constant 7,98 instead of 3,83 is much too high, suffers from the same evil. Terms with  $1/T^2$  and  $1/T^3$  may occur neither in a theoretical, nor in an empirical formula. At low temperatures  $\log p$  must approach to  $-A/T$ , whereas according to the formula mentioned  $\log p$  would approach to  $-A'/T^3$ , which is an absurdity. Already in the neighbourhood of  $2^{\circ},4$  it gives much too low values for  $p$ <sup>1)</sup>.

If we wish to construct a theoretical formula, which is valid throughout the *whole* region, the variability of  $a$  with  $T$ , of  $b$  with  $T$  and  $v$ , and of  $v_1$  with  $T$  must be taken into account over a great range; in any case an equation arises of the form  $\log p = -\frac{A}{T} + B \log T + C + DT + ET^2 \dots$ . But this problem is particularly difficult for Helium with its deviating behaviour at lower temperatures.

In the following table the values of  $p$  have been calculated according to both formulae from 0,1 to 0,1 degree. At the same times the values of  $F = \frac{T dp}{p dt} = T \frac{d \log p}{dt}$  are then obtained. For from our equation

$$\log^{10} p = -\frac{A}{T} + C + DT \text{ follows immediately } F = \left( \frac{A}{T} + DT \right) \times 2,3026,$$

of which the terms  $\frac{A}{T}$  and  $DT$  are, therefore, already known from the calculation of  $\log^{10} p$ . The accurate knowledge of  $F$  is necessary for the calculation of

$$\left. \begin{aligned} L &= T \frac{dp}{dt} (v_2 - v_1) = F \times p (v_2 - v_1) = F \times W \\ \text{and} \quad \lambda &= L - p (v_2 - v_1) = L - W = (F - 1) W \end{aligned} \right\} \dots (11)$$

which quantities we shall calculate in § 4.

<sup>1)</sup> Cf. also Note 2) added to Table IV.

TABLE II.  
a. Values of  $\rho$  and  $F$  between  $0^\circ$  and  $4^\circ.2$ .

$T$	$\frac{3.8308}{T}$	$0.2107 T$	$\log^{10} \rho^{mm}$	$\rho^{mm}$	$F: 2.3026$	$F$
0	$\infty$	0	$-\infty$	0	$\infty$	$\infty$
0.5	7.6616	0.1054	- 4.6518	0.0 <sub>4</sub> 223	7.7670	17.88
0.6	6.3847	0.1264	- 3.3539	0.0 <sub>3</sub> 443	6.5111	14.99
0.7	5.4726	0.1475	- 2.4207	0.0 <sub>2</sub> 380	5.6201	12.94
0.8	4.7885	0.1686	- 1.7155	0.0193	4.9571	11.41
0.9	4.2564	0.1896	- 1.1624	0.0688	4.4460	10.24
1.0	3.8308	0.2107	- 0.7157	0.1924	4.0415	9.306
1.1	3.4825	0.2318	- 0.3463	0.4505	3.7143	8.553
1.2	3.1923	0.2528	- 0.0351	0.9224	3.4451	7.933
1.3	2.9468	0.2739	+ 0.2315	1.704	3.2207	7.416
1.4	2.7363	0.2950	0.4631	2.90 $\bar{5}$	3.0313	6.980
1.5	2.5539	0.3161	0.6666	4.641	2.8700	6.608
1.6	2.3943	0.3371	0.8472	7.034	2.7314	6.289
1.7	2.2534	0.3582	1.0092	10.21	2.6116	6.013
1.8	2.1282	0.3793	1.1555	14.31	2.5075	5.774
1.9	2.0162	0.4003	1.2885	19.43	2.4165	5.564
2.0	1.9154	0.4214	1.4104	25.73	2.3368	5.381
2.1	1.8242	0.4425	1.5227	33.32	2.2667	5.219
2.2	1.7413	0.4635	1.6266	42.33	2.2048	5.077
2.3	1.6656	0.4846	1.7234	52.89	2.1502	4.951
2.4	1.5962	0.5057	1.8139	65.1 $\bar{5}$	2.1019	4.840
2.5	1.5323	0.5268	1.8989	79.23	2.0591	4.741
2.6	1.4734	0.5478	1.9788	95.24	2.0212	4.654
2.7	1.4188	0.5689	2.0545	113.4	1.9877	4.577
2.8	1.3681	0.5900	2.1263	133.8	1.9581	4.509
2.9	1.3210	0.6110	2.1944	156.5 $\bar{5}$	1.9320	4.449
3.0	1.2769	0.6321	2.2596	181.8	1.9090	4.396
3.1	1.2357	0.6532	2.3219	209.8	1.8889	4.349
3.2	1.1971	0.6742	2.3815	240.7	1.8713	4.309
3.3	1.1608	0.6953	2.4389	274.7	1.8561	4.274
3.4	1.1267	0.7164	2.4941	312.0	1.8431	4.244
3.5	1.0945	0.7375	2.5474	352.7	1.8320	4.218
3.6	1.0641	0.7585	2.5988	397.0	1.8226	4.197
3.7	1.0354	0.7796	2.6486	445.2	1.8150	4.179
3.8	1.0081	0.8007	2.6970	497.7	1.8088	4.165 $\bar{5}$
3.9	0.9823	0.8217	2.7438	554.4	1.8040	4.154
4.0	0.9577	0.8428	2.7895	615.9	1.8005	4.146
4.1	0.9343	0.8639	2.8340	682.3	1.7982	4.141
4.2	0.9121	0.8849	2.8772	753.7	1.7970	4.138

b. Values of  $\rho$  and  $F$  between  $3^{\circ}.5$  and  $5^{\circ}.2$ .

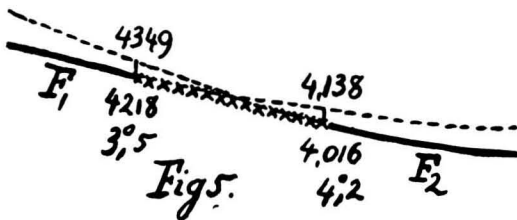
$T$	$\frac{4.9874}{T}$	$0.1325 T$	$\log^{10} \rho^{mm}$	$\rho^{mm}$	$F: 2.3026$	$F$
3.5	1.4250	0.4638	2.5471	352.5	1.8888	4.349
3.6	1.3854	0.4770	2.5999	398.0	1.8624	4.288
3.7	1.3479	0.4903	2.6507	447.4	1.8382	4.233
3.8	1.3125	0.5035	2.6993	500.4	1.8160	4.182
3.9	1.2788	0.5168	2.7463	557.6	1.7956	4.135
4.0	1.2469	0.5300	2.7914	618.6	1.7769	4.091
4.1	1.2164	0.5433	2.8352	684.2	1.7597	4.052
4.2	1.1875	0.5565	2.8773	753.9	1.7440	4.016
4.3	1.1599	0.5698	2.9182	828.3	1.7297	3.983
4.4	1.1335	0.5830	2.9578	907.4	1.7165	3.952
4.5	1.1083	0.5963	2.9963	991.5	1.7046	3.925
4.6	1.0824	0.6095	3.0336	1080	1.6937	3.900
4.7	1.0611	0.6228	3.0700	1175	1.6839	3.877
4.8	1.0390	0.6360	3.1053	1274	1.6750	3.857
4.9	1.0178	0.6493	3.1398	1380	1.6671	3.839
5.0	0.9975	0.6625	3.1733	1490	1.6600	3.822
5.1	0.9779	0.6758	3.2062	1608	1.6537	3.808
5.2	0.9591	0.6890	2.2382	1731	1.6481	3.795

Hence we find for the value of  $F$  at the critical temperature  $5^{\circ}.19$ :

$$F_k = 1,6487 \times 2,3026 = 3,7963 = \underline{3,80}.$$

The almost identical values of  $\rho$  between  $3^{\circ}.5$  and  $4^{\circ}.2$ , obtained with the two formulae, may now simply be averaged. The values of  $F$  should be treated in another way. Care should be taken, that the two parts  $F_1$  and  $F_2$  in the added graphical representation (see Fig. 5) pass continuously into each other (denoted by the line  $\times\times\times\times$ ). For this

purpose the differences  $\Delta$  should only be gradually decreased from 35 (between  $3^{\circ}.2$  and  $3^{\circ}.3$ ) to 27 (between  $4^{\circ}.4$  and  $4^{\circ}.5$ ). Cf. Table c.



## c. Adjusted values between 3°5 and 4°2.

<i>T</i>	<i>p</i> <sub>1</sub>	<i>p</i> <sub>2</sub>	<i>p</i>	<i>F</i> <sub>1</sub>	<i>F</i> <sub>2</sub>	<i>F</i>
3.2	240.7	—	240.7	4.309 <sup>Δ</sup>	—	4.309 <sup>Δ</sup>
3.3	274.7	—	242.7	4.274 <sup>35</sup>	—	4.274 <sup>35</sup>
3.4	312.0	—	312.0	4.244 <sup>30</sup>	—	4.242 <sup>32</sup>
3.5	352.7	352.5	352.6	4.218 <sup>26</sup>	4.349 <sup>Δ</sup>	4.212 <sup>30</sup>
3.6	397.0	398.0	397.5	4.197 <sup>21</sup>	4.288 <sup>61</sup>	4.183 <sup>29</sup>
3.7	445.2	447.4	446.3	4.179 <sup>18</sup>	4.233 <sup>55</sup>	4.154 <sup>29</sup>
3.8	497.7	500.4	499.1	4.165 <sup>14</sup>	4.182 <sup>51</sup>	4.125 <sup>29</sup>
3.9	554.4	557.6	556.0	4.154 <sup>11</sup>	4.135 <sup>47</sup>	4.096 <sup>29</sup>
4.0	615.9	618.6	617.2	4.146 <sup>8</sup>	4.091 <sup>44</sup>	4.067 <sup>29</sup>
4.1	682.3	684.2	683.3	4.141 <sup>5</sup>	4.052 <sup>39</sup>	4.038 <sup>29</sup>
4.2	753.7	753.9	753.8	4.138 <sup>3</sup>	4.016 <sup>36</sup>	4.009 <sup>29</sup>
4.3	—	828.3	828.3	—	3.983 <sup>33</sup>	3.980 <sup>29</sup>
4.4	—	907.4	907.4	—	3.952 <sup>31</sup>	3.952 <sup>28</sup>
4.5	—	991.5	991.5	—	3.925 <sup>27</sup>	3.925 <sup>27</sup>

2. The second Virial-Coefficient *B* and the vapour volume *v*<sub>2</sub>.

For the calculation of the values of *v*<sub>2</sub> (required for  $W = p(v_2 - v_1)$ ), the values of *B* in

$$pv_2 = RT + \frac{B}{v_2} \dots \dots \dots (12)$$

should be rather accurately known. Only at very low temperatures (to about 0°<sup>7</sup>)  $pv_2 = RT$  may be put; the deviations soon become pretty great for Helium, much greater than for "ordinary" substances. The values of *B*, calculated in the following table, have been derived from the formula

$$10^6 B = (-44.9 + 2,032 T) e^{\frac{1.155}{T}}, \dots \dots \dots (13)$$

the coefficients of which has been calculated from the pretty certain values **512** at 0°C.; **0** at 22°<sup>1</sup> abs. (*Boyle point*); and **-47,7** at 4°<sup>23</sup> abs.; marked in the subjoined table with an asterisk and printed in bold type. This theoretical formula was derived<sup>1)</sup> by me at the time in the form

$$B = (RT \varphi_1 b_k - \varphi_2 a_k) e^{\frac{\alpha}{T} - \frac{\alpha}{T_k}} = (-\beta_1 + \beta_2 T) e^{\frac{\alpha}{T}},$$

the efficiency of which has been tested by me by a number of substances

<sup>1)</sup> J. de Ch. ph. 17 (1919), p. 266—324. Cf. also Zustandsgl. p. 21 et seq.

(He, H<sub>2</sub>, Ne, Ar, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>3</sub>Cl). The available material of facts for *Helium* is combined in Table III.

TABLE III. 1)

<i>T</i>	$10^6 B_{exp.}$	$10^6 B_{formula}$
673 (400° C.)	+ 1126 (from 457 H.O.)	+ 1325
573 (300° ..)	+ 986 ( .. 470 .. )	+ 1125
473 (200° ..)	+ 854 ( .. 493 .. )	+ 919
373 (100° C.)	+ 701 (from 513 H.O.); K.O. 493 at 100°.35	+ 716*
323 ( 50° ..)	+ 619 ( .. 523 .. )	+ 614*
293 ( 20° ..)	+ 534 ( .. 448 K.O.)	+ 553*
*273.09 ( 0° ..)	+ 512 (K.O.; 529 H.O.)	+ 512
169.52	+ 337 (from 543 K.O.)	+ 302
90.34	+ 176 ( .. 532 .. )	+ 141
69.86	+ 100.3 (v. A.; K.O.)	+ 98.7*
56.53	(+ 96.0) (from 464 K.O.)	+ 71.4
55.68	(+ 97.0) ( .. 476 P.; K.O.)	+ 69.6
*22.1 (BOYLE-p.)	0 (v. A.; K.O. grafically from †)	0
20.55 } 53 } 51 } 48 }	- 4.2 } - 9.0 } † (v.A.; K.O.) } - 9.1 } - 7.4 (from - 99 Pal.; K.O.) }	- 3.4 (20°.5)*
20.37	(+ 3.0) ( .. + 40 K.O.*)	- 3.7
18.22 } 16.55 }	(- 24.4) } (- 24.5) } † (v.A.; K.O.) }	- 8.4 ) - 12.1 )
14.27	- 11.4 (from - 211 K.O.*)	- 17.3
4.71 } 59 } 29 }	- 45.9 } - 46.9 } (from D <sub>2</sub> M.; Cr.; K.O.; Sw.) } - 47.0 (from - 2990 K.O.**)	- 45.2 } - 45.7 } * - 47.4 }
*4.23	- 47.7 ( .. D <sub>2</sub> M. - Sw.)	- 47.7

1) The addition: "from 457 H. O." means that 457 must be multiplied by  $1 + 0,0036618 t$ . For these values refer to  $p v_2 = RT \left(1 + \frac{B'}{v}\right)$ , so that our  $B = RTB' = (273 + t) : 273 \cdot B' = (1 + 0,0036618 t) B'$ . ( $R = 1 : 273.09$  in norm. units).

H.O. means HOLBORN en OTTO 1924; K.O. = K. ONNES, Comm. 102a; K.O.\* =

In particularly good agreement are the values (marked with an asterisk) at 100°, 50° and 20° C., at 69°<sub>9</sub> abs., 20°<sub>5</sub> abs. (—4.2 against calculated —3.4) and the three values at about 4°<sub>5</sub> abs. The values at 56° and at 20°<sub>4</sub>, 18°<sub>2</sub> and 16°<sub>6</sub>, placed between parentheses, on the other hand, fall outside the schema, also of a graphical representation, and may, therefore, be ignored. We may, therefore, safely use the formula (13) for the calculation of the  $B$ -values at some temperatures below the critical temperature, occurring in Comm. 172*b*. These values, and those below 2°<sub>3</sub> are necessary for the determination of  $D_2$  for

TABLE IV.

$T$	$10^6 RT$	$p_{form.}^{atm.}$	$10^6 B_{form.}$	$10^6 v_2 calc.$	$10^4 D_2 calc.$	$10^4 D_2$ Comm. 172 <i>b</i>	$10^6 pv_2$ <i>calc.</i>	$\Delta$ BOYLE in %
5.19	19005	2.2605	(—42.9) <sup>1)</sup>	2572 <sup>3)</sup>	693.8 <sup>3)</sup>	693.0 <sup>3)</sup>	5815	69.4
4.71	17247	1.5592	—45.2	6800	262.4	269.9	1060.10	38.6
4.59	16808	1.4092	—45.7	7737	230.6	238.9 <sup>4)</sup>	1090.10	35.2
4.23	15489	1.0197	—47.7	1090.10	163.7	163.7	1111.10	28.2
4.22	15453	1.0111	—47.8	1098.10	162.5	161.8	1112.10 <sup>5)</sup>	28.0
3.90	14281	0.7316	—49.7	1499.10	119.0	117.6	1097.10	23.2
3.30	12084	0.3614	—54.2	2810.10	63.50	64.35	1016.10	16.0
2.56	9374	0.1169	—62.3	7288.10	24.48	(20.79)	8520	9.11
2.37	8678	0.08088	—65.2 <sup>2)</sup>	9916.10	17.99	(13.68) <sup>2)</sup>	8020	7.58
2.30	8422	0.06959	—66.5	1125.10 <sup>2)</sup>	15.86	(11.59)	7830	7.03
2.29	8386	0.06812	—66.7	1146.10 <sup>2)</sup>	15.57	—	7804	6.94
2.21	8093	0.05699	—68.1	1330.10 <sup>2)</sup>	13.42	—	7580	6.34
2.10	7690	0.04384	—70.4	1657.10 <sup>2)</sup>	10.77	—	7264	5.54
1.93	7067	0.02788	—74.5	2425.10 <sup>2)</sup>	7.358	—	6761	4.33
1.92	7031	0.02709	—74.8	2484.10 <sup>2)</sup>	7.184	—	6729	4.30
1.59	5822	0.008897	—86.2	6392.10 <sup>2)</sup>	2.792	—	5687	2.32
1.28	4687	0.001997	—104	2325.10 <sup>3)</sup>	0.7675	—	4643	0.94
1.20	4394	0.001214	—111	3595.10 <sup>3)</sup>	0.4964	—	4363	0.70

ibid. Comm. 102*c*; K.O.\*\* = ibid. Comm. 119*a*; P.; K.O. = PENNING and K.O., Comm. 165*c*; Pal.; K.O. = PALACIOS MARTINEZ and K.O., Comm. 164; v. A.; K.O. = VAN AGT and K.O., Comm. 176*b*, p. 28 (1925); M.; Cr.; K.O.; Sw. = MATHIAS, CROMMELIN, K.O. and SWALLOW, Comm. 172*b*. Compare also KEESOM and K.O., Arch. Néerl. IX, N<sup>o</sup>. 1 (1925).

Cf. the notes 1, 2, 3, 4 and 5 of Table IV on the following page.

the calculation of the diameter. For this reason the values of  $v_2$ , calculated from (12), resp.  $D_2=4:22416 v_2=178,444 \cdot 10^{-6} : v_2$  (see § 2, 1st Part, after (4)), are inserted in the foregoing table by the side of those of  $B$ ; and besides those of  $pv_2$ , to judge about the deviations from the law of BOYLE.

After these preliminary calculations (as said before, necessary for the calculation of the diameter, see § 3), we have again inserted all the quantities of Table IV in Table V, but now over the whole region and from 0.1 to 0,1 degree. The values of  $v_2$  (and  $D_2$ ) above  $4^{\circ},7$  cannot be calculated accurately by means of (12), because then the vapour volumes become too small. We have, therefore, calculated the values of  $D_2$  (and of  $D_1$ ) at these temperatures from formulae for  $\frac{1}{2}(D_1+D_2)$  and  $\frac{1}{2}(D_1-D_2)$  (see § 3), and then  $v_2$  (and  $v_1$ ) from  $D_2$  (and  $D_1$ ). The values of  $v_2$  and  $D_2$  from  $4^{\circ},3$  to  $4^{\circ},7$  (inclusive), placed between brackets, have been calculated in the same way; it is seen that they differ but little from the values calculated from (12), which may be considered to be very accurate; since the values of  $B$  on which they are based (see Table III) have been calculated directly from the *observed* values of  $D_2$  according to Comm. 172*b*, and therefore refer to the saturation line.

The deviations from the law of BOYLE are comparatively great, and negligible only up to  $0^{\circ},7$ . Above this  $pv_2$  may no longer be put equal to  $RT$ . The same applies to  $v_2-v_1$  (see § 3), for which  $v_2$  may be put only to  $0^{\circ},9$ . For benzene the deviation from the law of BOYLE at  $70^{\circ}$  ( $m=0,61$ ) is  $2\%$  (Zustandsgl. p. 156); this already amounting to almost  $15\%$  for Helium at the same reduced temperature ( $T=3^{\circ},2$ )! This is

1) This value is no longer valid on the saturation line, as the critical volume can no longer be considered as large. Terms should then still be added with  $C : v_2^2$  etc. From  $B = (RT_k - p_k v_k) v_k$  is calculated the correct value  $-34,0$ .

2) The  $B$ -values, used by M.; Cr.: K.O. and Sw. for the calculation of their  $D_2$ -values, viz. resp.  $-93,40$ ,  $-98,05$  and  $-99,87$  (according to a kind communication from Dr. CROMMELIN), are much too great negative in my opinion, at least on the saturation line. But chiefly the  $p$ -values, used by the said authors, viz. resp.  $71,10$ ,  $46,37$  and  $38,46$  mm. (instead of  $88,84$ ,  $61,47$  and  $52,89$  mm., calculated according to (10), cf. also Table IIa), are much too low. For the experimental value at  $2^{\circ},24$  is already  $51$  mm. (calculated  $46,6$ , see Table I); the pressure at the *higher* temperature  $2^{\circ},30$ , therefore, *cannot possibly* be  $= 38,46$ ! The reason is, that the authors have used the formula of Comm. 147*b* (cf. § 1), which is quite inadmissible at these temperatures. It is chiefly these erroneous  $p$ -values, that have caused the great errors in the  $D_2$ -values calculated by them, through which e.g.  $11,59$  was found for  $10^4 D_2$  at  $2^{\circ},30$  instead of  $15,86$ , which value is almost  $50\%$  higher.

3) Calculated from the diameter, see further.

4) These values have been directly observed; they are in pretty good agreement with the calculated values. The following values have been calculated; the first three are still correct, but the last three are, in my opinion, entirely wrong. Comp. Note 2).

5) Here a maximum for  $pv_2$  at  $m=T: T_k = 4,22 : 5,19 = 0,81$  is duly found. For "ordinary" substances this maximum lies at the same place: for benzene e.g. at  $m=0,80$  (Cf. Zustandsgl. p. 255, Fig. 8). It appears from Table IX, that the maximum of  $W = p(v_2-v_1)$  is situated at  $m=0,73$  ( $T=3^{\circ},8$ ), against  $0,77$  for benzene.



owing to the fact, that with equal  $m$  the deviations are about proportional to the *reduced pressures*  $\varepsilon = p : p_k$ . And since for Benzene  $\varepsilon = 548 : 36486 = 0,015$  at  $m = 0,61$ , and for the Helium  $= 231,4 : 1718 = 0,135$ ,

TABLE V.

$T$	$m$	$10^6 RT$	$p^{atm.}$	$10^6 B$	$10^6 v_2$	$10^4 D_2$	$10^6 pv_2$	$\Delta$ BOYLE (‰) ( $RT - pv_2$ ): : $RT \times 100$
0	0	0	0	$\infty$	$\infty$	0	0	0
0.5	0.09634	1831	0.072934	-442	$6241 \cdot 10^7$	0.0429	1831	0.0339
0.6	0.1156	2197	0.065825	-299	$3772 \cdot 10^6$	0.0347	2197	0.0236
0.7	0.1349	2563	0.054995	-226	$5131 \cdot 10^5$	0.0235	2563	0.017
0.8	0.1541	2929	0.042533	-183	$1156 \cdot 10^5$	0.015	2927	0.055
0.9	0.1734	3296	0.049053	-155	$3636 \cdot 10^4$	0.049	3292	0.13
1.0	0.1927	3662	0.032532	-136	$1443 \cdot 10^4$	0.12	3653	0.26
1.1	0.2119	4028	0.035928	-122	$6764 \cdot 10^3$	0.26	4010	0.45
1.2	0.2312	4394	0.021214	-111	$3595 \cdot 10^3$	0.50	4363	0.70
1.3	0.2505	4760	0.02242	-103	$2101 \cdot 10^3$	0.85	4711	1.03
1.4	0.2698	5127	0.023822	-96.0	$1322 \cdot 10^3$	1.35	5054	1.42
1.5	0.2890	5493	0.026107	-90.4	$8827 \cdot 10^2$	2.02	5391	1.86
1.6	0.3083	5859	0.029255	-85.7	$6180 \cdot 10^2$	2.89	5721	2.37
1.7	0.3276	6225	0.01343	-81.8	$4500 \cdot 10^2$	3.97	6043	2.92
1.8	0.3468	6591	0.01883	-78.4	$3377 \cdot 10^2$	5.28	6359	3.52
1.9	0.3661	6957	0.02557	-75.4	$2608 \cdot 10^2$	6.84	6668	4.16
2.0	0.3854	7324	0.03386	-72.8	$2059 \cdot 10^2$	8.67	6970	4.83
2.1	0.4046	7690	0.04384	-70.4	$1657 \cdot 10^2$	10.77	7264	5.54
2.2	0.4239	8056	0.05570	-68.3	$1356 \cdot 10^2$	13.16	7552	6.26
2.3	0.4432	8422	0.06959	-66.5	$1125 \cdot 10^2$	15.86	7830	7.03
2.4	0.4624	8788	0.08572	-64.8	$9452 \cdot 10$	18.88	8102	7.81
2.5	0.4817	9155	0.1043	-63.2	$8022 \cdot 10$	22.24	8367	8.61
2.6	0.5010	9521	0.1253	-61.8	$6882 \cdot 10$	25.93	8623	9.43
2.7	0.5202	9887	0.1492	-60.5	$5944 \cdot 10$	30.02	8869	10.3
2.8	0.5395	10253	0.1761	-59.3	$5172 \cdot 10$	34.50	9108	11.2
2.9	0.5588	10619	0.2059	-58.1	$4535 \cdot 10$	39.35	9338	12.1

which is 9 times greater, the  $7^{1/2}$  times greater deviation for Helium is accounted for.

TABLE V (Continued).

$T$	$m$	$10^6 RT$	$p^{atm.}$	$16^6 B$	$10^6 v_2$	$10^4 D_2$	$10^6 pv_2$	$\Delta$ BOYLE (%) ( $RT - pv_2$ ): : $RT \times 100$
3.0	0.5780	10985	0.2392	-57.0	3997.10	44.64	9561	13.0
3.1	0.5973	11352	0.2761	-56.0	3545.10	50.34	9772	13.9
3.2	0.6166	11718	0.3167	-55.1	3147.10	56.70	9967	14.9
3.3	0.6358	12084	0.3614	-54.2	2810.10	63.50	1016.10	16.0
3.4	0.6551	12450	0.4105	-53.4	2516.10	70.92	1033.10	17.0
3.5	0.6744	12816	0.4639	-52.6	2261.10	78.92	1049.10	18.2
3.6	0.6936	13182	0.5230	-51.8	2034.10	87.73	1064.10	19.3
3.7	0.7129	13549	0.5872	-51.1	1833.10	97.35	1076.10	20.6
3.8	0.7322	13914	0.6567	-50.4	1655.10	107.8	1087.10	21.9
3.9	0.7515	14281	0.7316	-49.7	1499.10	119.0	1097.10	23.2
4.0	0.7707	14647	0.8121	-49.1	1359.10	131.3	1104.10	24.7
4.1	0.7900	15013	0.8991	-48.5	1232.10	144.8	1108.10	26.2
4.2	0.8093	15380	0.9918	-47.9	1119.10	159.5	1111.10	27.8
4.3	0.8285	15746	1.090	-47.3	1019.10 (1021.10)	175.1 (174.8)	1112.10	29.4
4.4	0.8478	16112	1.194	-46.8	9271 (9298)	192.5 (191.9)	1109.10	31.2
4.5	0.8671	16478	1.305	-46.2	8425 (8461)	211.8 (210.9)	1102.10	33.1
4.6	0.8863	16844	1.421	-45.7	7649 (7658)	233.3 (233.0)	1088.10	35.4
4.7	0.9056	17210	1.546	-45.2	6887 (6878)	259.1 (259.4)	1064.10	38.2
4.8	0.9249	17577	1.676	(-44.7)	6108	292.1	1024.10	41.8
4.9	0.9441	17943	1.816	(-44.2)	5340	334.1	9697	46.0
5.0	0.9634	18308	1.961	(-43.8)	4564	391.0	8950	51.1
5.1	0.9827	18675	2.116	(-43.3)	3744	476.6	7922	57.6
5.19	1	19005	2.261	(-42.9)	2572	693.8	5815	69.4

From  $pv_2 = RT + \frac{B}{v_2}$  follows  $\Delta = (RT - pv_2) : RT = -\frac{B}{v_2} : RT$ . And  $B$  being  $= RTb_g - a_g$  for large volumes,  $\Delta$  becomes  $= (a_g - RTb_g) : RTv_2$ , in which  $a_g$  and  $b_g$  are the values of  $a$  and  $b$  at the temperature  $T$

and at  $v = \infty$ . As  $a$  is practically independent of the volume,  $a$  may simply be written instead of  $a_g$ . Now at lower temperatures  $\leq a_k$  may be substituted for  $a - RTb_g = \theta a_k - RTb_g$  (in which for ordinary substances  $\theta$  is always  $> 1$ , but for Helium  $< 1$ ); hence we get ( $m = T : T_k$ ):

$$\Delta \leq \frac{a_k}{RTv_2} \leq \frac{a_k \cdot p}{RT \cdot pv_2} \leq \frac{a_k \cdot p}{(RT)^2} \leq \frac{a_k \cdot \epsilon p_k}{m^2 (RT_k)^2}$$

With  $p_k = \frac{1}{27} \frac{a_k}{b_k^2}$ ,  $RT_k = \frac{8}{27} \frac{a_k}{b_k}$  this becomes:

$$\Delta \leq \frac{27}{64} \frac{\epsilon}{m^2} \dots \dots \dots (14)$$

From this follows, therefore, that with equal  $m$ ,  $\Delta$  is "about" proportional to  $\epsilon$ . With his usual lack of thoroughness NERNST writes simply  $\epsilon$  for  $[RT - p(v_2 - v_1)] : RT$ , which does not differ much from  $\Delta$  up to near  $T_k$ . This is only correct in approximation at  $m^2 = 27/64$ ,  $m = 0,63$ , but of course not with arbitrary values of  $m$ . How great the differences, accordingly, are between NERNST and reality, especially at higher reduced temperatures, appears from the table on p. 257 of my "Zustands-gleichung".

Let us take as example Helium at  $m = 0,5$  ( $T = 2^\circ,6$ ). Here  $\epsilon$  is  $= 0,1253 : 2,261 = 0,0554$ , so that  $\Delta$  is somewhat  $< \frac{27}{64} \times 0,2216$ , or  $< 0,109$ . We really found  $9,43 \%$ , i.e.  $0,094$ .

The explanation, why  $\epsilon$  for Helium is e.g. 9 times greater than for benzene at the same value of  $m$  (see above), follows from the approximated vapour pressure formula  $-\log \epsilon = f \left( \frac{1}{m} - 1 \right)$  or  $\epsilon = e^{-f \left( \frac{1}{m} - 1 \right)}$ . Now  $f = 3.16$  for Helium at  $m = 0,61$ , and  $f = 6,59$  for benzene <sup>1)</sup>, so that  $\epsilon$  becomes resp.  $= e^{-2,02}$  and  $e^{-4,20}$ , i.e. for Helium  $e^{2,18} = 8,8 = 9$  times greater than for benzene.

The same ratios are found for  $v_2 : v_1$  (see Table IX). Thus e.g.  $v_2 : v_1$  is only  $= 23$  for Helium ( $3^\circ,26$ ) at  $m = 0,63$ , this ratio being  $300$  at the boiling-point ( $80^\circ \text{C.}$ ) of benzene ( $m$  likewise  $= 0,63$ ).

**3. The values of  $1/2(D_1 + D_2)$  and  $1/2(D_1 - D_2)$  in the neighbourhood of the critical temperature.**

For the calculations of the so-called "Diameter" we only use those data, that are sufficiently far from the maximum liquid density at  $2^\circ,3$ ; we take the following values of  $D_1$  and  $D_2$  (see also Table IV).

<sup>1)</sup> This depends again on the family of the substances, as  $f = 8\gamma$ , and  $\gamma$  is  $= 0.9$  or  $1$  for ordinary substances and  $< 0.5$  for Helium.

TABLE VI.

$T$	$D_1$ (C.172 <sup>b</sup> )	$D_{2ca.c.}$ (Table IV)	$\frac{1}{2}(D_1 + D_2)$	Ibid formula
*3.30	0.1395	0.0063 <sup>5</sup>	0.0729 <sup>25</sup>	0.0729 <sup>25</sup>
*3.90	0.1311	0.0119 <sup>0</sup>	0.0715 <sup>0</sup>	0.0715 <sup>0</sup>
4.22	0.1255	0.0162 <sup>5</sup>	0.0708 <sup>75</sup>	0.0708 <sup>54</sup>
*4.23	0.1253	0.0163 <sup>7</sup>	0.0708 <sup>35</sup>	0.0708 <sup>35</sup>
4.59	0.1165	0.0230 <sup>6</sup>	0.0697 <sup>8</sup>	0.0702 <sup>06</sup>
4.71	0.1139	0.0262 <sup>4</sup>	0.0700 <sup>7</sup>	0.0700 <sup>18</sup>

From the values at 3°,30, 3°,90 and 4°,23, marked by us with an asterisk, we calculate:

$$10^4 \cdot \frac{1}{2}(D_1 + D_2) = 857,41 - 51,60 T + 3,868 T^2,$$

which, accordingly, gives a course *convex* towards the  $T$ -axis (*concave* at lower temperatures, where  $D_1$  quite predominates with its maximum). We may also write:

$$\underline{10^4 \cdot \frac{1}{2}(D_1 + D_2) = 693,79 + 11,45 (T_k - T) + 3,868 (T_k - T)^2,} \quad (15)$$

or also with  $T = mT_k$ :

$$10^4 \cdot \frac{1}{2}(D_1 + D_2) = 693,79 + 59,426(1 - m) + 104,19(1 - m)^2,$$

or with  $D = d \times D_k$ , in which  $d$  is, therefore, the reduced density:

$$\underline{\frac{1}{2}(d_1 + d_2) = 1 + 0,085654(1 - m) + 0,15017(1 - m)^2.}$$

From this follows:

$$\gamma = 0,085654 + 0,30034(1 - m),$$

which, at  $T_k$  ( $m=1$ ) gives  $\gamma=0,086$ , but at  $T=3^\circ,90$  ( $m=0,75$ ) already  $0,86 + 0,075 = 0,161$ , i.e. almost *double* the value!

We find for  $D_k$ :

$$\underline{10^4 D_k = 693,8.} \quad (\text{Comm. 172b: } 693,0).$$

If the values, found for  $\frac{1}{2}(D_1 + D_2)$  according to the formula, are assumed to be correct, and also the calculated values of  $D_2$ , the value  $1254^6 = 1255$  (exp. 1255), follows for  $10^4 D_1$  at 4°,22, the value  $1173^{52} = 1174$  (exp. 1165) at 4°,59, and the value  $1137^{96} = 1138$  (exp. 1139) at 4°,71. Accordingly it follows that there is no objection to calculating  $D_2$  to 4°,7 from the values of  $B$  and  $p$  calculated by us, which we, accordingly, have done in Table V. The corresponding values of  $D_1$  between 3°,3 and 4°,7 can then be calculated from (15).

Past  $4^{\circ},71$  up to  $5^{\circ},19$  recourse must be had to a theoretical formula for  $\frac{1}{2}(D_1 - D_2)$ , valid in the neighbourhood of  $T_k$ , viz. (cf. also Zustandsgl. p. 332 and 346)

$$\frac{\frac{1}{2}(D_1 - D_2)}{\sqrt{T_k - T}} = a' - \beta'(T_k - T) + \delta'(T_k - T)^2 \dots$$

For the calculation of the coefficients  $a'$ ,  $\beta'$  and  $\delta'$  we use the following data.

TABLE VI<sup>a</sup>.

$T$	$D_1$	$D_2$	$D_1 - D_2$	$\sqrt{T_k - T}$	$\frac{1}{2}(D_1 - D_2) : \sqrt{\phantom{x}}$
4.23	0.1253	0.01637	0.10893	0.9798	555.9
4.59	0.11735	0.02306	0.09429	0.7746	608.6
4.71	0.1138	0.02624	0.08756	0.6928	631.9

And from this follows:

$$\frac{1}{2}(D_1 - D_2) : \sqrt{T_k - T} = 753.77 - 301.67(T_k - T) + 99.54(T_k - T)^2, \quad (16)$$

for which may also be written, with  $D = d \times D_k$ :

$$\begin{aligned} \frac{1}{2}(d_1 - d_2) : \sqrt{T_k - T} &= 1.0865 - 0.43481(T_k - T) + 0.14347(T_k - T)^2 \\ &= 1.0865 - 2.2567(1 - m) + 3.8645(1 - m)^2, \end{aligned}$$

hence

$$\frac{1}{2}(d_1 - d_2) : \sqrt{1 - m} = 2.475 - 5.141(1 - m) + 8.804(1 - m)^2.$$

The constant term  $a$  is therefore = 2,475. This is 3,6 to 4 for ordinary substances ( $\gamma = 0,9$  to 1), about 3 for argon ( $\gamma = 0,75$ ) and 2 for "ideal" substances ( $a$  and  $b$  constant,  $\gamma = 0,5$ ). Hence  $a$  is always  $-4\gamma$ .

Now for Helium  $s = R T_k : p_k v_k = 0,019005 : 0,005815 = \underline{3,268}$  (see Table V), and  $s$  being =  $8\gamma : (1 + \gamma)$ , the value 0,69 would follow for the "theoretic" value of  $\gamma$  for Helium, so that  $4\gamma$  becomes = 2,76, which is, therefore, here slightly more than 2,475. For the quantity  $r = v_k : b_k$  we find for Helium  $0,002572 : 0,001051 = \underline{2,447}$ . For  $rs$  we find for Helium the general value 8, as  $3,268 \times 2,447 = \underline{7,997} = 8,00$ . (Compare also Zustandsgl. p. 141). [For "ideal" substances  $s$  is =  $\frac{8}{3}$  and  $r$  is = 3; for ordinary substances  $s$  is = 3,6 to 4,  $r$  is = 2,22 to 2].

From (15) and (16) the following values are now calculated between  $4^{\circ},3$  and  $5^{\circ},2$ ; those of  $D_2$  and  $v_2$  have already been recorded in Table V.

As regards  $D_1$ , we have already the values between  $4^{\circ},3$  and  $5^{\circ},19$  in the following Table. Further we have the experimental material of Comm. 170 (K. ONNES and BOKS) and 172b (M., CR., K.O. and Sw.) between  $1^{\circ},2$  and  $4^{\circ},2$  (Table VIII), and also the values calculated by us in Table A of the first Part of this paper.

TABLE VII.

$T$	$10^4 \cdot \frac{1}{2}(D_1+D_2)$	$10^4 \cdot \frac{1}{2}(D_1-D_2)$	$10^4 D_1$	$10^4 D_2$	$10^6 v_1$	$10^6 v_2$
4.3	707.0	532.2	1239	174.8	1440	10206
4.4	705.2	513.3	1219	191.9	1464	9298
4.5	703.5	492.6	1196	210.9	1492	8461
4.6	701.9	468.9	1171	233.0	1524	7658
4.7	700.3	440.9	1141	259.4	1564	6878
4.8	698.8	406.7	1106	292.1	1614	6108
4.9	697.4	363.3	1061	334.1	1682	5340
5.0	696.1	305.1	1001	391.0	1782	4564
5.1	694.9	218.2+	913.1	476.6	1954	3744
5.19	693.8	0	693.8	693.8	2572	2572

The values of  $D_1$  according to Comm. 170 and 172*b* are the following. Those of Comm. 170 have all been increased by 7 units of the last decimal, in accordance with the last correction in Comm. 172*b* on account of an improved determination of the normal volume.

TABLE VIII.

$T$	$10^4 D_1$	$T$	$10^4 D_1$	$T$	$10^4 D_1$
1.20	1459	2.10	1464 <sup>5</sup>	2.56	1457
1.28	1459	2.21	1466	3.30	1395
1.59	1460	2.30	<b>1496</b> (max)	3.90	1311
1.92	1462	2.37	1466	4.22	1255
1.93	1462				

From this, interpolations can easily be made from 1<sup>o</sup>,2 to 3<sup>o</sup>,3. But between 3<sup>o</sup>,3 and 4<sup>o</sup>,2 some  $D_1$ -values must still be calculated. This is done by subtracting the values of  $D_2$  from the values of  $D_1 + D_2$  calculated according (15), through which the following table is obtained.

TABLE VIII<sup>a</sup>.

$T$	$10^4 (D_1+D_2)$	$10^4 D_2$	$10^4 D_1$	$T$	$10^4 (D_1+D_2)$	$10^4 D_2$	$10^4 D_1$
3.3	1458.5	63.5	1395	3.8	1434.4	107.8	1327
3.4	1453.4	70.9	1382	3.9	1430.0	119.0	1311
3.5	1448.4	78.9	1369	4.0	1425.8	131.3	1294
3.6	1443.6	87.7	1356	4.1	1421.7	144.8	1277
3.7	1438.9	97.4	1342	4.2	1417.8	159.5	1258

#### 4 The values of $W = p(v_2 - v_1)$ , $L$ and $\lambda$ .

Now the whole material is complete for the determination of  $W$  (the values of  $p$  in atm. should be taken from Table V),  $L = F \times W$ , and

TABLE IX.

$T$	$10^4 D_2$	$10^4 D_1$	$10^6 v_2$	$10^6 v_1$	$v_2 : v_1$	$10^6 W = 10^6 \cdot p(v_2 - v_1)$	$F$	$10^5 L$ (norm. units)	$L'$ (Gr. cal.)	$10^5 \lambda = L - W$ (norm. units)
0	0	1458 <sup>6</sup>	$\infty$	1223 <sup>4</sup>	$\infty$	0	$\infty$	3230	17.53	3230
0.5	0.0 <sub>4</sub> 29	1458 <sup>0</sup> (min)	6241.10 <sup>7</sup>	1223 <sup>9</sup> (max)	5.10 <sup>7</sup>	1831	17.88	3274	17.77	3091
0.6	0.0 <sub>3</sub> 47	1458 <sup>1</sup>	3772.10 <sup>6</sup>	1223 <sup>9</sup>	3.10 <sup>6</sup>	2197	14.99	3293	17.87	3073
0.7	0.0 <sub>2</sub> 35	1458 <sup>1</sup>	5131.10 <sup>5</sup>	1223 <sup>8</sup>	4.10 <sup>5</sup>	2563	12.94	3317	18.00	3061
0.8	0.015	1458 <sup>2</sup>	1156.10 <sup>5</sup>	1223 <sup>7</sup>	1.10 <sup>5</sup>	2927	11.41	3340	18.12	3047
0.9	0.049	1458 <sup>3</sup>	3636.10 <sup>4</sup>	1223 <sup>6</sup>	3.10 <sup>4</sup>	3292	10.24	3371	18.29	3042
1.0	0.12	1458 <sup>5</sup>	1443.10 <sup>4</sup>	1223 <sup>5</sup>	12.10 <sup>3</sup>	3652	9.306	3399	18.44	3034
1.1	0.26	1458 <sup>7</sup>	6764.10 <sup>4</sup>	1223 <sup>3</sup>	55.10 <sup>2</sup>	4009	8.553	3429	18.61	3028
1.2	0.50	1459 <sup>0</sup>	3595.10 <sup>3</sup>	1223 <sup>1</sup>	29.10 <sup>2</sup>	4362	7.933	3459	18.77	3023
1.3	0.85	1459 <sup>3</sup>	2101.10 <sup>3</sup>	1222 <sup>8</sup>	172.10	4708	7.416	3491	18.95	3021
1.4	1.3	1459 <sup>6</sup>	1322.10 <sup>3</sup>	1222 <sup>5</sup>	108.10	5049	6.980	3524	19.12	3019
1.5	2.0	1460 <sup>0</sup>	8827.10 <sup>2</sup>	1222 <sup>2</sup>	722	5384	6.608	3558	19.31	3019 (min)
1.6	2.9	1460 <sup>5</sup>	6180.10 <sup>2</sup>	1221 <sup>8</sup>	506	5710	6.289	3591	19.49	3020
1.7	4.0	1460 <sup>9</sup>	4500.10 <sup>2</sup>	1221 <sup>4</sup>	369	6027	6.013	3624	19.67	3021
1.8	5.3	1461 <sup>4</sup>	3377.10 <sup>2</sup>	1221 <sup>0</sup>	277	6336	5.774	3658	19.85	3022
1.9	6.8	1462 <sup>0</sup>	2608.10 <sup>2</sup>	1220 <sup>5</sup>	214	6637	5.564	3693	20.04	3029
2.0	8.7	1563 <sup>0</sup>	2059.10 <sup>2</sup>	1219 <sup>7</sup>	169	6929	5.381	3728	20.23	3035
2.1	11	1464	1657.10 <sup>2</sup>	1219	136	7211	5.219	3763	20.42	3042
2.2	13	1466	1357.10 <sup>2</sup>	1217	111	7484	5.077	3800	20.60	3052 (point of inflection)
2.3	16	1469 (max)	1125.10 <sup>2</sup>	1215 (min)	93	7744	4.951	3834 (point of inflection)	20.80	3060
2.4	19	1465	9452.10	1218	78	7998	4.840	3871	21.01	3071
2.5	22	1460	8022.10	1222	66	8239	4.741	3906	21.20	3082
2.6	26	1454	6882.10	1227	56	8469	4.654	3941	21.39	3094
2.7	30	1448	5944.10	1232	48	8685	4.577	3975	21.57	3107
2.8	34 <sup>5</sup>	1442	5172.10	1237	42	8890	4.509	4009	21.75	3120
2.9	39	1435	4535.10	1244	36	9081	4.449	4040	21.92	3132

TABLE IX (Continued).

$T$	$10^4 D_2$	$10^4 D_1$	$10^6 v_2$	$10^6 v_1$	$v_2 : v_1$	$10^6 W =$ $10^6 \cdot p (v_2 - v_1)$	$F$	$10^5 L$ (norm. units)	$L'$ (Gr. cal.)	$10^5 \lambda = L - W$ (norm. units)
3.0	45	1427	3997.10	1250	32	9262	4.396	4072	22.09	3146
3.1	50	1418	3545.10	1258	28	9440	4.349	4105	22.28	3161
3.2	57	1407	3147.10	1268	25	9565	4.309	4122	22.36	3165
3.3	63 <sup>5</sup>	1395	2810.10	1279	22	9693	4.274	4143	22.48	3174
3.4	71	1382	2516.10	1291	19	9798	4.242	4156	22.55	<b>3176 (max)</b>
3.5	79	1369	2261.10	1303	17	9884	4.212	<b>4163 (max)</b>	<b>22.59</b>	3175
3.6	88	1356	2034.10	1316	15	9950	4.183	4162	22.58	3167
3.7	97	1342	1833.10	1320	14	9982	4.154	4147	22.50	3149
3.8	108	1327	1655.10	1345	12	<b>9985 (max)</b>	4.125	4119	22.35	3120
3.9	119	1311	1499.10	1361	11	9971	4.096	4084	22.16	3087
4.0	131	1294	1359.10	1379	10	9917	4.067	4033	21.89	3041
4.1	145	1277	1232.10	1397	8.8	9821	4.038	3966	21.52	2984
4.2	159 <sup>5</sup>	1258	1119.10	1418	7.9	9692	4.009	3886	21.08	2917
4.3	175	1239	1020.10	1440	7.1	9559	3.980	3804	20.64	2848
4.4	192	1219	9284	1464	6.4	9337	3.952	3697	20.06	2762
4.5	211	1196	8443	1492	5.7	9071	3.925	3570	19.37	2661
4.6	233	1171	7654	1524	5.0	8711	3.900	3399	18.45	2527
4.7	259	1141	6882	1564	4.4	8222	3.877	3185	17.28	2363
4.8	292	1106	6108	1614	3.8	7532	3.857	2905	15.76	2152
4.9	334	1061	5340	1682	3.2	6643	3.839	2550	13.84	1886
5.0	391	1001	4564	1782	2.6	5456	3.822	2085	11.32	1539
5.1	477	913	3744	1954	1.9	3788	3.808	1442	7.83	1063
5.19	694	694	2572	2572	1	0	3.795	0	0	0

$\lambda = L - W$  (see (11) in § 1). The values of  $D_2$  and  $v_2$ , already given in Table V, have been repeated in the foregoing Table IX, as also the values of  $F$  from Table II. To reduce  $L$  expressed in normal units to  $L'$  in gr. cal., we must multiply by 542,63 (see § 2 of the first Part of this paper).

When we represent the values, found for  $L$  in this table — which, as appears from what precedes, have been calculated with the greatest care



and accuracy from the available data concerning  $p$ ,  $B$ ,  $D_2$  and  $D_1$  — by a graph, we obtain a continuous curve, which has a *maximum* at  $3^\circ,5$ , and a *point of inflection* at  $2^\circ,3$ . The presence of this point had already been stated in § 4 of the first Part. The maximum had necessarily to appear, because the initial course at  $T=0$  is *ascending*. (cf. there formula (9)).

On the contrary the initial course of  $\lambda$  is *descending* (loc. cit.), and leads necessarily to a *minimum* (at about  $1^\circ,5$ ), because  $\lambda$  in conformity with  $L$  has a *maximum* at almost the same place ( $3^\circ,4$ ). Of course there is again a *point of inflection* between minimum and maximum, and this about at the same temperature as that of the point of inflection of  $L$  (c.f. Fig. 2).

DANA and KAMERLINGH ONNES (loc. cit., cf. § 1 of the first Part) also made a calculation of the values of  $L$  between  $3^\circ$  and  $5^\circ$ , but in consequence of the less accurate values of  $dp/dt$  and  $v_2-v_1$ , used by them, they only obtained a rough approximation (see the following table). They find, indeed, also the maximum at  $3^\circ,5$ , but their values at  $3^\circ$ ,  $3^\circ,5$  and  $4^\circ$  are slightly too high. That at  $5^\circ$  is almost identical with ours, the value at  $4^\circ,5$ , viz. 16,0, being quite incongruous. In their graphic representation they have, accordingly, substituted 19 (i.e. 4,75 gr. cal. per gr. He) for this value (i. e. 4 gr. kal. per gr. He), through which they have obtained a continuous curve (loc. cit. p. 1056).

The values found experimentally by DANA and K.O. are, indeed, in harmony, as far as order of magnitude is concerned (see Table X), with our calculated values; but the place of the maximum can hardly be ascertained from them, since their values are about constant between  $2^\circ$  and  $3^\circ,5$ .

TABLE X.

	$T=0$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.19
$L_{theor.}$ v. $L.$	= 17.5	17.8	18.4	19.3	20.2	21.2	22.1	22.6	21.9	19.4	11.3	0
Ibid. D.; K.O.	—	—	—	—	—	—	23.2	24	22.8	(16.0?)	11.2	0
$L_{exp.}$	„	—	—	—	21.8	22.3	22.4	22.6	22.2	20.2	—	—

More accurate measurements will be required to establish the course experimentally with more certainty. From their measurements the authors also conclude (see the footnote on p. 1057), that there happens "*something particular*" in the neighbourhood of  $2^\circ,3$  (which happens to be exactly the place of the maximum liquid-density). But the degree of accuracy of their experiments does not allow them here either to elucidate this point further. But after our considerations and calculations we now know, that really something particular happens here, i. e. the occurrence of a *point of inflection*, below which the course of  $L$  is *convex* with regard to the temperature-axis, and above which it becomes *concave*, proceeding to the maximum at  $3^\circ,5$ .

As we have seen, the appearance of this maximum can be explained in a *perfectly natural* way, of which the clue lies in formula (9), viz. (augmented by  $R$ , to transform  $d\lambda/dt$  to  $dL/dt$ )

$$\frac{dL}{dt} = -\frac{\beta a_0}{v_0^2} + R = -0,003127 + 0,003662 = +0,000535,$$

through which, owing to the abnormally low value of  $a_0$  for Helium,  $dL/dt$  proves to be *positive*, instead of negative, as in all other substances. Consequently the appearance of this maximum does not give in my opinion — in opposition to DANA and K. O.'s opinion — the slightest support to the calculations of VERSCHAFFELT cited in their paper, which are in connection with a possible “degeneration of energy” of the liquid at very low temperatures. The degeneration of energy is, in my opinion, not only *improbable* (it does not even explain the maximum and minimum in the liquid density), but its assumption is also *unnecessary*, because the ordinary theory, taking the deviating behaviour of the quantity  $a$  into consideration (rise instead of fall on increasing temperature), accounts for all the particularities, even in detail.

Also the abnormally low specific heat, but this will be treated on a subsequent occasion.

*Tavel sur Clarens, Suisse, Summer 1926.*

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