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**Physics.** — “*On the solid state.*” III. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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10. Before proceeding to the discussion of the course of the  $p$ - $T$ -line liquid-solid, we shall first adduce some more material to prove our statements. For the values assumed by us of  $a$ ,  $b$ , etc. (Comp. II p. 27) we shall namely successively calculate, besides the already calculated isotherm for  $T=9$  (see I and II), also the isotherms of  $100^\circ$ ,  $128^\circ$ ,  $144^\circ$ ,  $160^\circ$ ,  $200^\circ$  and  $400^\circ$  (all absolute temperatures), in order to show that on increase of temperature they really present the shapes and transitions indicated by us. (see the Plate of Part I, fig. 1—3).

The accurate course of all these isotherms  $p = f(v)$  for  $T=0$ , 9, 100, etc. has been indicated on the Plate belonging to this paper. In view of the available dimensions the scale of the pressure-values had to be somewhat reduced, which appears particularly for the critical isotherm ( $T=400$ ), where  $p_c = 400$ , i.e.  $400 \times 41,2 = 16480$  atms. — or after division by 100 (see II, p. 27<sup>1)</sup>) = 165 atms., which is rendered comparatively small in the drawing. The values of  $v$  have not been indicated further than  $v=3$  (300), so that the last maximum no longer falls inside the limits of the drawing.

The isotherm  $T=0$  (comp. II, p. 34) is indicated by a line of alternate dashes and dots<sup>2)</sup>. Further the locus of the maxima  $D$  and of the minima  $C$ , which passes through the point of inflection  $I$ , where  $C$  and  $D$  coincide, has been indicated by an ordinary dotted line. We may remind the reader that the solid phase (for so far as it is realizable) always lies on the portion  $CD$  of the isotherms, the liquid

<sup>1)</sup> So all the pressure values of the following tables must still be multiplied by 0,412; all the values of volume by 100.

<sup>2)</sup> The values of  $p$  in the curvilinear part  $ED$  have been calculated from the equation  $p = \frac{q_0}{-\Delta b} - \frac{a}{v^2} = 6400 - \frac{a}{v^2}$  [see II, p. 31, formule (8), which apparently applies to all the points between  $E$  and  $D$ , where  $\varphi = \frac{1}{\theta} = \infty$ , so that  $(p + a/v^2)(-\Delta b) = q_0$  (see II, p. 31-32)]. The corresponding values of  $\beta$  may be calculated for this part from the relation  $v=b$  holding there (for  $v = \frac{1+\beta}{v-b}(-\Delta b) = \infty$ ), so that  $\beta$  becomes  $= \frac{b_1 - v}{-\Delta b}$ . (See form. (11) of II, p. 35).

phase on the portion  $EF$ . The vapour phase (between  $A$  and  $B$ ) lies outside the limits of our drawing.

The locus of the minima in  $E$  and of the maxima in  $B$ , which passes through the critical point  $K$ , where  $B$  and  $E$  coincide, has not been indicated in our drawing.

Nor are the pressures of coexistence liquid-solid, solid-vapour, liquid-vapour indicated by horizontal lines; only for  $T=0$  the pressure of coexistence liquid-solid is indicated ( $p=1000$ ), whereas that for solid-vapour coincides with the axis  $p=0$ .

$$\underline{T=100.}$$

Now with  $\theta = \frac{200}{3200} = \frac{1}{16}$  the formula (3<sup>a</sup>) [see II, p. 26] becomes:

$$\frac{\beta^2}{1-\beta^2} = 32000 \times \left(\frac{1}{16}\right)^{3/2} e^{-16 \frac{e^p}{\varphi}} = 500 e^{-16 \frac{e^p}{\varphi}},$$

hence

$$\log^{10} \frac{1-\beta^2}{\beta^2} = -4,250 + 0,4343 \varphi - \log^{10} \varphi,$$

while for  $p$  we find  $p = 400 \varphi - \frac{2700}{v^2}$  (see II, p. 28).

$\varphi = \frac{1+\beta}{v-b}(-\Delta b)$	$\log^{10} \frac{\beta^2}{1+\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	$\beta$	$v$	$p$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
23	4,377	$2,38 \times 10^4$	$1 - \frac{1}{48000}$	0,54	+ 60
17	1,903	80,0	0,994	0,56	-1760
16	1,495	31,3	0,98	0,57	-1920
15	1,089	12,3	0,96	0,58	-1900
13	0,282	1,91	0,81	0,66	- 920
12	-0,117	0,763	0,66	0,74	- 130
11	-0,514	0,306	0,48	0,83	+ 440
10	-0,907	0,124	0,33	0,90	+ 670
9,5	-1,102	0,0791	0,27	0,93	+ 600
9	-1,293	0,0509	0,22	0,96	+ 660
7	-2,055	0,00881	0,093	1,03	+ 260
5	-2,777	0,00167	0,041	1,08	- 300
3	-3,424	0,000265	0,016	1,16	- 800
2	-3,682	0,000208	0,014	1,25	- 940
1	-3,815	0,000153	0,012(min.)	1,50	- 800
0,5	-3,732	0,000185	0,014	2,0	- 470
0,25	-3,539	0,000289	0,017	3,0	- 190
0,1	-3,206	0,000622	0,025	6,1	- 32
0,03	-2,726	0,00188	0,043	18	+ 4,0
0,02	-2,542	0,00287	0,054	27	4,4
0,01	-2,245	0,00568	0,075	55	3,1
$10^{-3}$	-1,249	0,0563	0,23	620	0,39
$10^{-1}$	-0,250	0,563	0,60	8000	0,040
$10^{-5}$	0,750	5,63	0,92	96000	0,004
$10^{-6}$	1,750	56,3	0,991	$10^6$	0,0004
0	$\infty$	$\infty$	1	$\infty$	0

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The minimum value of  $\beta$  for  $v = 1,5$  ( $\varphi = 1$ ), which amounted only to  $10^{-38}$  for  $T = 9$ , has now already risen to  $0,012 = 10^{-2}$ .

From the approximate relation  $\frac{v^3}{(v-1)^2} = \frac{2a}{RT} = 27$ , which holds for  $B$  and  $C$  if  $\beta = 0$  (see II, p. 33), we should find  $v_C = 1,28$  and  $v_B = 24,9$ . And as  $v = 1 + \frac{1}{2\varphi}$  for  $\beta = 0$ , we have  $\varphi_C = 1,8$  and  $\varphi_B = 0,021$ , while then the corresponding values of  $p$  are further  $p_C = -930$ ,  $p_B = 4,0$ . So these approximate values agree pretty well with the exact values of the table.

$T = 128.$

Now with  $\theta = \frac{256}{3200} = \frac{1}{12,5}$  ( $3^a$ ) becomes:

$$\frac{\beta^2}{1-\beta^2} = 32000 \times \left(\frac{1}{12,5}\right)^{3/2} e^{-12,5} \frac{e}{\varphi},$$

or

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -2,569 + 0,4343 \varphi - \log^{10} \varphi,$$

whereas further  $p = 512 \varphi \frac{2700}{v^2}$ .

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$\varphi$	$\log^{10} \frac{\beta^2}{1-\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	$\beta$	$v$	$P$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
17	.3,584	3830	$1 - \frac{1}{7700}$	0,56	+ 61
12	1,563	36,6	0,987	0,59	- 1630
11	1,167	14,7	0,97	0,61	- 1730
10	0,774	5,94	0,93	0,63	- 1600
9	0,386	2,43	0,84	0,68	- 1210
8	0,002	1,01	0,71	0,75	- 660
7	- 0,374	0,423	0,55	0,84	- 260
6	- 0,741	0,181	0,39	0,92	- 120
5	- 1,096	0,0801	0,27	0,99	- 190
4	- 1,434	0,0268	0,19	1,05	- 380
3	- 1,743	0,0181	0,13	1,12	- 610
2	- 2,001	0,00997	0,099	1,23	- 770
1	- 2,135	0,00733	0,085(min.)	1,5	- 690
0,5	- 2,051	0,00390	0,094	2,0	- 390
0,25	- 1,858	0,0139	0,12	3,2	- 140
0,1	- 1,525	0,0290	0,17	6,8	- 7,8
0,05	- 1,246	0,0567	0,23	13	+ 10,1
0,04	- 1,154	0,0702	0,26	17	+ 10,7
0,03	- 1,033	0,0927	0,29	22	+ 10,0
0,01	- 0,565	0,273	0,46	74	4,6
0,001	0,432	2,70	0,85	930	0,51
0,0001	1,431	27,0	0,98	9900	0,051
0	$\infty$	$\infty$	1	$\infty$	0

The minimum value of  $\beta$  is almost 0,1 at this temperature.

In the maximum at  $D$  the pressure is now negative, so that we are already above the triple-point temperature at  $128^\circ$ .

$$T = 144.$$

With  $\theta = \frac{288}{3200} = \frac{9}{100}$  the equation (3<sup>a</sup>) becomes:

$$\frac{\beta^2}{1-\beta^2} = 32000 \times \left( \frac{9}{100} \right)^{3/2} e^{-\frac{100}{9} e^{\frac{\varphi}{\varphi}}}$$

hence

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -1,889 + 0,4343 \varphi - \log^{10} \varphi,$$

while  $p$  is calculated from  $p = 576 \varphi - \frac{2700}{v^2}$ .

$\varphi$	$\log^{10} \frac{\beta^2}{1-\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	$\beta$	$v$	$p$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
14,5	3,149	2810	$1 - \frac{1}{5600}$	0,57	+ 16
{ 10	{ 1,454	{ 28,4	{ 0,98	{ 0,61	{ -1550
{ 9	{ 1,065	{ 11,6	{ 0,96	{ 0,63	{ -1640
{ 8	{ 0,682	{ 4,81	{ 0,91	{ 0,66	{ -1510
7	0,306	2,02	0,82	0,72	-1160
6	-0,061	0,868	0,68	0,80	-770
{ 5	{ -0,416	{ 0,383	{ 0,53	{ 0,89	{ -530
{ 4	{ -0,754	{ 0,176	{ 0,39	{ 0,98	{ -510
{ 3	{ -1,063	{ 0,0865	{ 0,28	{ 1,07	{ -620
{ 2,5	{ -1,201	{ 0,0629	{ 0,24	{ 1,13	{ -690
{ 2	{ -1,321	{ 0,0477	{ 0,21	{ 1,20	{ -733
{ 1,5	{ -1,414	{ 0,0386	{ 0,19	{ 1,30	{ -730
1	-1,455	0,0351	0,18 (min)	1,5	-620
0,5	-1,371	0,0426	0,20	2,1	-320
0,25	-1,178	0,0663	0,25	3,4	-90
0,10	-0,846	0,143	0,35	7,6	+ 10,7
{ 0,07	{ -0,731	{ 0,186	{ 0,40	{ 10,8	{ + 17,3
{ 0,06	{ -0,641	{ 0,229	{ 0,43	{ 12,7	{ + 17,9
{ 0,05	{ -0,566	{ 0,271	{ 0,46	{ 15,4	{ + 17,4
0,01	0,115	1,30	0,75	89	5,4
0,001	1,111	12,9	0,96	980	0,57
0,0001	2,111	129	0,996	10000	0,058
0,	$\infty$	$\infty$	1	$\infty$	$\infty$

Again  $\beta_{min}$  is larger, now already = 0,18. The maximum at  $D$  and the minimum at  $C$  have drawn very near to each other; we shall presently see, that at  $160^\circ$  the coinciding takes place in

a point of inflection  $I = C, D$ . (Cf. Fig. 3 of the plate of part I).

$$T = 160.$$

With  $\theta = \frac{320}{3200} = \frac{1}{10}$  we have now:

$$\frac{\beta^2}{1-\beta^2} = 32000 \times (1/10)^{1/2} e^{-10} \frac{e^{\varphi}}{\varphi},$$

or

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -1,338 + 0,4343 \varphi - \log^{10} \varphi.$$

The pressure is given by  $p = 640 \varphi - \frac{2700}{v^2}$ .

$\varphi$	$\log^{10} \frac{\beta^2}{1-\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	$\beta$	$v$	$p$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
12,5	2,994	986	$1 - \frac{1}{2000}$	0,58	— 19
8	1,233	17,1	0,97	0,64	— 1530
7	0,857	7,20	0,94	0,67	— 1536
6	0,490	3,09	0,87	0,72	— 1350
5	0,135	1,36	0,76	0,80	— 1060
4	— 0,203	0,627	0,62	0,89	— 832
3,5	— 0,362	0,435	0,55	0,95	— 775
3	— 0,512	0,308	0,49	1,005	— 753
2,5	— 0,650	0,224	0,43	1,07	— 751
2	— 0,770	0,170	0,38	1,15	— 745
1,5	— 0,862	0,137	0,35	1,28	— 700
1	— 0,904	0,125	0,33 (min.)	1,5	— 560
0,5	— 0,820	0,151	0,36	2,2	— 250
0,25	— 0,627	0,236	0,44	3,7	— 40
0,1	— 0,294	0,508	0,58	8,6	27,6
0,09	— 0,253	0,559	0,60	9,6	28,2
0,08	— 0,206	0,622	0,62	10,8	28,1
0,07	— 0,152	0,704	0,64	12,4	27,3
0,01	0,667	4,64	0,91	96	6,1
0,001	1,663	46,0	0,99	1000	0,64
0	$\infty$	$\infty$	1	$\infty$	0

(C,D)



The minimum value of  $\beta$  is  $= 0,33$ . The horizontal point of inflection  $I = C, D$  lies evidently in the neighbourhood of  $\varphi = 2,5$ ,  $v = 1,07$ ,  $p = -750$ .

At  $200^\circ$  not a trace is left of the horizontal point of inflection, and only the minimum  $E$  and the maximum  $B$  of the ordinary isotherm of VAN DER WAALS is to be seen, as will appear from a following table.

11. We shall, however, first give a survey of the situation of the maximum  $D$  and the minimum  $C$  at the different temperatures from  $T = 0$  to  $T = 160$  calculated by us.

	$T=0$	9	100	128	144	160
$\left\{ \begin{array}{l} \varphi_D \\ \varphi_C \end{array} \right.$	$\infty$	173	9,5	5,9	4,4	2,5
$\left\{ \begin{array}{l} \beta_D \\ \beta_C \end{array} \right.$	0	0,027	0,27	0,37	0,45	0,43
$\left\{ \begin{array}{l} v_D \\ v_C \end{array} \right.$	1	0,99	0,93	0,93	0,94	1,07
$\left\{ \begin{array}{l} p_D \\ p_C \end{array} \right.$	+ 3700	+ 3470	+ 690	- 120	- 500	- 750
	- 2700	- 2100	- 940	- 770	- 730	

As was said before, the locus of maxima and minima (one continuous curve, on which the point of inflection is also found) is indicated by a dotted line on the plate.

If we wish to know the data of the point of inflection accurately, we may calculate them from the formulae which I drew up in the before cited paper in the Arch. Teyler for a *critical* point (i. e. for every point where a maximum and a minimum in the isotherm  $p = f(v)$  coincide to a horizontal point of inflection), viz. (see loc. cit. p. 29 and 31):

$$\frac{v_c}{b_c} = 3 \frac{m^2}{3m^2 - n^2} ; \quad RT_c = \frac{8}{27} \frac{a}{b_c} \frac{1}{1 + \beta} \cdot \frac{n^2(3m^2 - 2n)}{m^5}, \quad (14)$$

in which  $m$  and  $n$  have the following signification:

$$\left. \begin{array}{l} m = 1 + \frac{1}{2} \beta(1 - \beta)(1 - \varphi)^2 \\ n = 1 + \frac{3}{4} \beta(1 - \beta)(1 - \varphi) + \frac{1}{8} \beta(1 - \beta)(1 - 3\beta^2)(1 - \varphi)^3 \end{array} \right\} . \quad (15)$$

Then the pressure is further determined by the equation of state, whereas  $\beta$  depends on  $T$  and  $\varphi$ , i. e. on  $T$  and  $v$ , according to formula (3) in II.

As  $\varphi_c = \frac{(-\Delta b)(1+\beta_c)}{v_c-b_c} = \frac{1/2(1+\beta_c)}{v_c-b_c}$ , and  $v_c = b_c$ , as follows from

the above equation for  $v_c$ , is evidently  $= 2b \times \frac{n}{3m^2-2n}$ , we have also:

$$\varphi_c = \frac{1}{4} \frac{1+\beta_c}{1-1/2\beta_c} \cdot \frac{3m^2-2n}{n}, \dots \dots \dots (14^a)$$

because  $b = b_1 + \beta\Delta b = 1 - 1/2\beta$ . Further with  $a = 2700$  and  $R = 2$  becomes:

$$T_c = \frac{400}{(1+\beta_c)(1-1/2\beta_c)} \frac{n^2(3m^2-2n)}{m^5} \dots \dots \dots (14^b)$$

We further remark (see also Teyler loc. cit.) that for  $\beta = 0$  or  $1$  the formulae (14) duly pass into  $v_c = 3b_c$  and  $RT_c = \frac{8}{27} \frac{a}{b_c}$ , as then  $m$  and  $n$  are  $= 1$ . It is true that for  $\beta = 1$  we find the expression  $\frac{8}{27} \frac{a}{b_c} \cdot \frac{1}{2}$  for  $RT_c$ , but as all the quantities refer to double molecular quantities,  $a = 4a_2$ ,  $b_c = 2b_2$  for  $\beta = 1$ , hence again  $RT_c = \frac{8}{27} \frac{a_2}{b_2}$ .

Now in order to calculate the exact values of  $\varphi_c$ ,  $\beta_c$ , and  $T_c$  from (14<sup>a</sup>) and (14<sup>b</sup>) in connection with (3), we may begin with assigning to  $\varphi$  an arbitrary value, which lies in the neighbourhood of the expected value of  $\varphi_c$ . With some values of  $\beta$ , which lie likewise in the neighbourhood of  $\beta_c$ , we may then calculate the corresponding values of  $m$  and  $n$ , and further those of  $\varphi_c$  and  $T_c$  from (14<sup>a</sup>) and (14<sup>b</sup>). Then we may determine  $\beta$  by interpolation in such a way, that the calculated value of  $\varphi$  corresponds with the assumed value. Then a value of  $T_c$  also belongs to this (to be found by interpolation).

Now we examine (from the above tables) what value of  $\beta$  corresponds with the assumed value of  $\varphi$  for the value of  $T_c$  determined just now (formula (3) in II). In this we shall, of course, have to interpolate again. The value of  $\beta$  thus found will not at once correspond with the value of  $\beta$  determined just now; we then repeat the whole calculation with another value of  $\varphi$ , till the two values of  $\beta$  correspond.

Thus we find e. g. with  $\varphi = 2,5$ :

$\varphi = 2,5$	$\beta = 0,4$	$m$	$n$	$f$	$T_c$	$f'$	$\varphi$
		1,27	0,6774	0,4838	172,8	5,144	2,251
	$\beta = 0,5$	1,281	0,6924	0,4916	174,8	5,114	2,557

in which for the sake of simplicity the expression  $\frac{n'(3m^2-2n)}{m^5}$  is represented by  $f$ , and  $\frac{3m^2-2n}{n}$  by  $f'$ .

We see at once that we must assume  $\beta = 0,48$  to find  $\varphi = 2,5$ , in correspondence with the assumed value. Then  $T_c$  would be  $= 174,4$ . But according to the table for  $160^\circ$  and that of  $200^\circ$  on p. 130, a value <sup>1)</sup> for  $\beta = 0,59$  corresponds to this with  $\varphi = 2,5$  which does not agree at all with  $\beta = 0,48$ . Hence the assumed value  $\varphi = 2,5$  is not correct.

Let us now assume  $\varphi = 2,6$ .

$$\varphi = 2,6 \left\{ \begin{array}{l} \beta = 0,4 \\ \beta = 0,5 \end{array} \right. \left\{ \begin{array}{l} m \\ n \\ f \\ T_c \end{array} \right\} \left\| \left\{ \begin{array}{l} f' \\ \varphi \end{array} \right. \right.$$

1,307	0,6481	0,4214	150,5	5,911	2,586
1,32	0,6680	0,4332	154,0	5,823	2,912

So to find  $\varphi = 2,6$ ,  $\beta$  must be  $= 0,404$ , to which corresponds  $T_c = 150,7$ . But as according to the tables  $\beta = 0,34$  corresponds with this, also  $\varphi = 2,6$  is not correct.

As for  $\varphi = 2,5$  the first found value of  $\beta$  is 0,11 units lower than the second, whereas for  $\varphi = 2,6$  the first is 0,064 higher, the accurate value of  $\varphi$  will lie in the neighbourhood of 2,55.

$$\varphi = 2,55 \left\{ \begin{array}{l} \beta = 0,43 \\ \beta = 0,44 \end{array} \right. \left\{ \begin{array}{l} m \\ n \\ f \\ T_c \end{array} \right\} \left\| \left\{ \begin{array}{l} f' \\ \varphi \end{array} \right. \right.$$

1,294	0,6643	0,4492	160,5	5,567	2,535
1,296	0,6654	0,4491	159,9	5,573	2,572

So if we take  $\beta = 0,434$ , we find  $\varphi = 2,55$ . Then  $T_c$  becomes  $= 160,3$ . To this corresponds  $\beta = 0,439$ , so that  $\varphi = 2,55$  is still slightly too small.

$$\varphi = 2,56 \left\{ \begin{array}{l} \beta = 0,40 \\ \beta = 0,45 \end{array} \right. \left\{ \begin{array}{l} m \\ n \\ f \\ T_c \end{array} \right\} \left\| \left\{ \begin{array}{l} f' \\ \varphi \end{array} \right. \right.$$

1,292	0,6600	0,4462	159,4	5,586	2,444
1,303	0,6643	0,4437	157,9	5,645	2,640

From this follows  $\beta = 0,430$ ,  $T_c = 158,5$ . This latter value, however, gives  $\beta = 0,421$ , so that  $\varphi = 2,56$  is slightly too high.

The accurate value of  $\varphi_c$  is therefore  $= 2,55 + \frac{5}{5+9} \times 0,01 = 2,554$ , to which belongs  $\beta_c = 0,433$ ,  $T_c = 159,6$ .

For  $v_c$  we find then further the value 1,064 from

<sup>1)</sup> It appears viz. from the two tables, in connection with that for  $144^\circ$ , that  $\beta$  in the neighbourhood of  $p = 2$  or  $3$  and  $T = 160$  increases by about 0,011 with every degree the temperature rises.

$v = 1 - \frac{1}{2} \left( \beta - \frac{1 + \beta}{\varphi} \right)$ , whereas  $p_c = 1630 - 2385 = \underline{-755}$  is found for  $p_c$  from  $p = 638,4 \varphi - \frac{2700}{v^2}$ .

So the values found theoretically agree perfectly with the values of the point of inflection derived from the table for  $160^\circ$ .

12. Now the tables for  $T=200$  and  $T=400$  may follow.

$$\underline{T = 200.}$$

With  $\theta = \frac{400}{3200} = \frac{1}{8}$  the formula for  $\beta$  becomes:

$$\frac{\beta^2}{1 - \beta^2} = 32000 \times \left(\frac{1}{8}\right)^{3/2} e^{-8} \frac{e^{\varphi}}{\varphi},$$

i.e.

$$\log^{10} \frac{\beta^2}{1 - \beta^2} = -0,3238 + 0,4343 \varphi - \log^{10} \varphi,$$

the pressure being given by  $p = 800 \varphi - \frac{2700}{v^2}$ .

$\varphi$	$\log^{10} \frac{\beta^2}{1 - \beta^2}$	$\frac{\beta^2}{1 - \beta^2}$	$\beta$	$v$	$p$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
9	2,631	427	$1 - \frac{1}{860}$	0,61	- 16
6	1,504	31,9	0,98	0,67	-1150
5	1,149	14,1	0,97	0,71	-1300
4	0,811	6,48	0,93	0,78	-1230
3	0,502	3,18	0,87	0,88	-1120
2	0,244	1,75	0,80	1,05	- 850
$1\frac{1}{2}$	0,152	1,42	0,77	1,21	- 660
1	0,110	1,29	0,75 (min)	1,5	- 400
0,5	0,194	1,56	0,78	2,4	- 72
0,25	0,387	2,44	0,84	4,3	+ 51
0,15	0,565	3,67	0,89	6,8	+ 62
0,10	0,720	5,24	0,92	10	+ 54
0,01	1,681	47,9	0,990	100	+ 7,7
0,001	2,677	475	$1 - \frac{1}{950}$	1000	0,80
0	$\infty$	$\infty$	1	$\infty$	0

The influence of the temperature on the values of  $\beta$  becomes stronger and stronger. Though  $\beta_{min}$  was only 0,33 at 160°, this value has now risen to 0,75. As we already remarked above, not a trace of a point of inflection is now found; only the minimum at  $E$  and the maximum at  $B$  of VAN DER WAALS' ordinary isotherm have been left.

$$T = 400.$$

For  $\beta$  we have in this case the relation

$$\frac{\beta^2}{1-\beta^2} = 32000 \times (1/4)^{3/2} e^{-4} \frac{e^{\theta}}{\varphi} = 4000 e^{-4} \frac{e^{\theta}}{\varphi},$$

as  $\theta = \frac{800}{3200} = \frac{1}{4}$ . So this yields:

$$\log^{10} \frac{\beta^2}{1-\beta^2} = 1,865 + 0,4343 \varphi - \log^{10} \varphi.$$

Then the value of  $p$  is further found from  $p = 1600\varphi - \frac{2700}{v^2}$ .

$\varphi$	$\log^{10} \frac{\beta^2}{1-\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	$\beta$	$v$	$p$
$\infty$	$\infty$	$\infty$	1	0,50	$\infty$
5	3,337	2175	$1 - \frac{1}{4400}$	0,70	2490
4	3,000	1000	$1 - \frac{1}{2000}$	0,75	1600
3	2,691	491	$1 - \frac{1}{980}$	0,83	910
2	2,433	271	$1 - \frac{1}{540}$	1,00	500
1	2,299	199	0,9975 (min)	1,5	400 (K)
0,5	2,383	242	$1 - \frac{1}{490}$	2,5	370
0,25	2,576	368	$1 - \frac{1}{740}$	4,5	270
0,1	2,908	810	$1 - \frac{1}{1600}$	10	140
0,01	3,869	7400	$1 - \frac{1}{15000}$	100	16
0,001	4,865	73300	$1 - \frac{1}{150000}$	1000	1,6
0	$\infty$	$\infty$	1	$\infty$	0

The temperature is here already so high, that the dissociation of the double molecules is almost complete; even for  $\varphi = 1$  the minimum value is still 0,9975. If  $\beta$  were exactly  $= 1$ , the isotherm of  $400^\circ$  would be the *critical* one (see the calculation in the previous paper); now it is *practically* identical with it. The critical pressure is 400, the critical volume  $= 1,5$ , i.e. just three times the volume of the simple molecules ( $= 0,5$ ). That the critical point is just found at the minimum value of  $\beta$ , is a mere chance. For in general when  $\beta = 1$ ,  $v_c$  is  $= 3 \times 2b_2$ . On the other hand the minimum of  $\beta$  is found at  $v_m = 2(b_1 - b_2) = b_1 - \Delta b$  (see before), so  $v_c = v_m$ , if  $6b_2 = 2(b_1 - b_2)$ , i.e.  $b_1 = 2 \times 2b_2$ . Now we assumed for our arbitrary substance  $b_1 = 1$ ,  $2b_2 = 0,5$ , so that this condition happens to be fulfilled.

It appears from the table and the plate, that there the former minimum at  $E$  and the maximum at  $B$  have coincided in a *horizontal point of inflection*, i.e. in the *critical point K*. For temperatures higher than  $400^\circ$  this point of inflection, too, will gradually disappear.

The different minima  $E$  and maxima  $B$  lie all on a curve, which passes through the critical point  $K$ , because there the maximum and minimum mentioned coincide. This locus is not indicated on the plate (see p. 121)

The following table gives a survey of the situation of these maxima and minima.

	$T=0$	9	100	128	144	160	200	400
$\left\{ \begin{array}{l} \varphi_L \\ \varphi_B \end{array} \right.$	$\infty$	186 <sup>+</sup>	16	1	9	7	5	1
$\left\{ \begin{array}{l} \beta_E \\ \beta_B \end{array} \right.$	0	0,0017 <sup>+</sup>	0,02	0,04	0,06	0,085	0,15	
$\left\{ \begin{array}{l} \beta_E \\ \beta_B \end{array} \right.$	1	$1 - \frac{1}{600}$	0,98	0,97	0,96	0,94	0,97	$1 - \frac{1}{400}$
$\left\{ \begin{array}{l} \beta_E \\ \beta_B \end{array} \right.$	0	2,210 <sup>-37</sup>	0,054	0,26	0,43	0,61	0,89	
$\left\{ \begin{array}{l} v_E \\ v_B \end{array} \right.$	0,50	0,506	0,57	0,61	0,63	0,67	0,71	1,5
$\left\{ \begin{array}{l} v_E \\ v_B \end{array} \right.$	$\infty$	298	27	17	13	10	7	
$\left\{ \begin{array}{l} p_E \\ p_B \end{array} \right.$	-4400	-3840	-1920	-1730	-1640	-1540	-1300	+400
$\left\{ \begin{array}{l} p_E \\ p_B \end{array} \right.$	0	+0,030	+4,4	+11	+18	+28	+62	

In a fourth continuation the discussion of the general course of the  $p, T$ -line liquid-solid (the line  $SM$  in Fig. 4 of I) will follow. As to the termination point of this line at  $T = 0$  (absolute), this was already fully discussed in II, § 8 (p. 31—36).

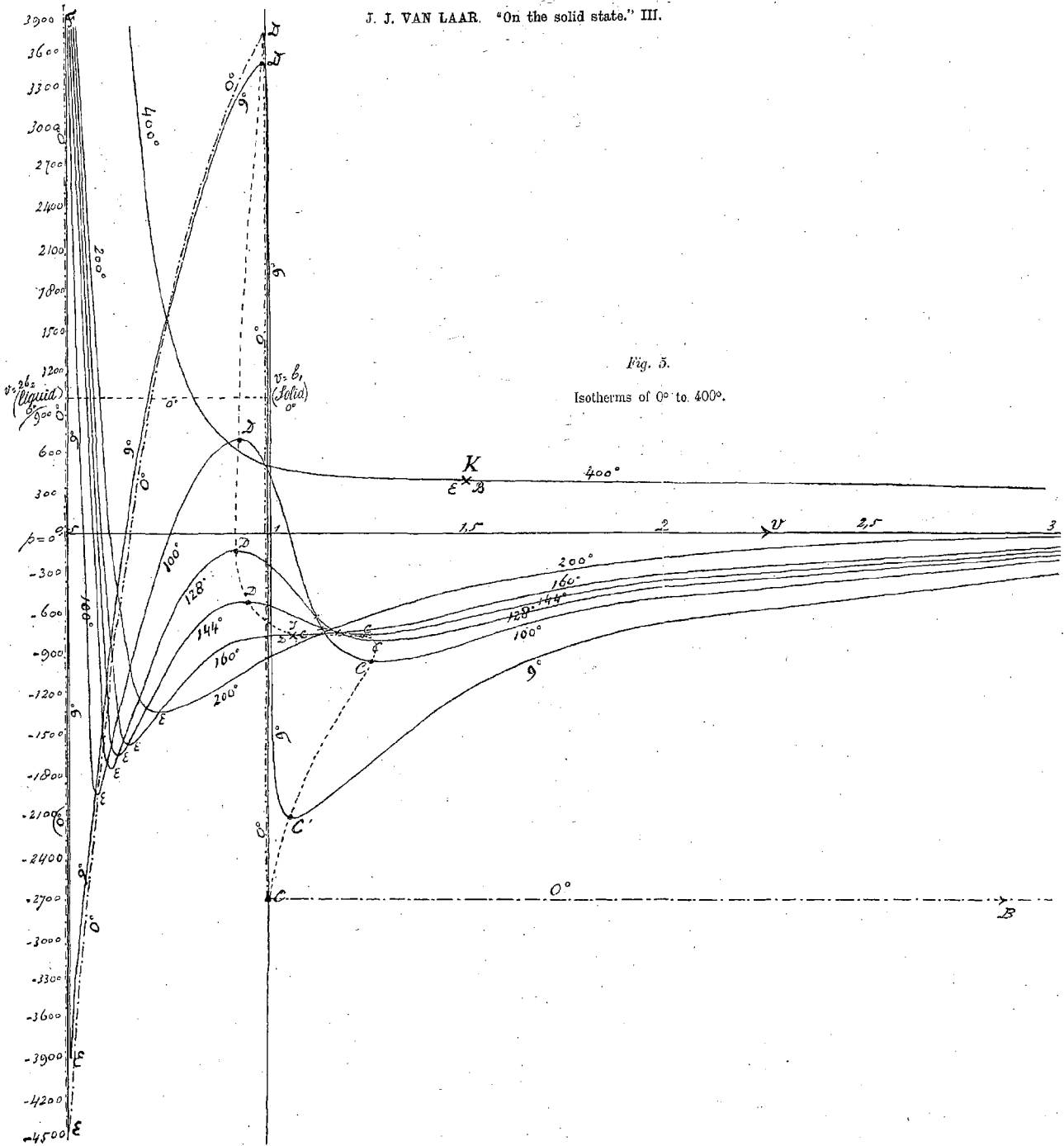


Fig. 5.

Isotherms of  $0^\circ$  to  $400^\circ$ .