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Δb positive.

24. Up to now we have considered the case Δb *negative.* Then the coexistence-curve liquid-solid proceeds from high pressure-values at $T=0$, with a maximum in the neighbourhood of $T=0$, either to a horizontal point of inflection E,D, at the same time *critical point liquid-solid,* where the two phases become identical, and where the minimum E of the isotherm coincides with the maximum D (see inter alia fig. 20 of V) — or to the neighbourhood of a horizontal point of inflection D,C, where the maximum D coincides with the minimum C.

In the example chosen by us, the first thing takes place when $-\Delta b < 0{,}454$; the second when $-\Delta b > 0{,}454$. For $-\Delta b = 0{,}454$, in the transition case, E, D, and C coincide all three.

For the intersection of the coexistence-curve of liquid-solid and that of vapour-liquid, so that a triple-point S arises, it is required that the said critical point E,D or the point of inflection D,C is found at a negative pressure, as the pressure in the triple point has mostly a very slight positive value. In our example e.g. this occurs for $-\Delta b = 0{,}5$ (fig. 14). Then S lies at about $^1/_4\ T_c$.

Now if Δb is *positive,* all this changes. Then the coexistence-curve ascends from below (see fig. 23—25) from low pressures, intersects in favourable cases (Δb large) the line vapour-liquid in a triple-point S, and again terminates in a *critical point* E,D solid-liquid. The curve, however, never terminates in a point of inflection D,C, as for Δb negative, when $-\Delta b > 0{,}454$. But it arises very low down from such a point [or rather in its neighbourhood, because only at somewhat higher temperature the first coexistence solid-liquid begins (see fig. 20 of V)].

So for Δb *negative* the course is *from* the axis $T=0$ to a critical point E,D or close to a point of inflection D,C (according to the value of $-\Delta b$), thus running from *above downward,* with (beyond the pressure maximum near $T=0$) always *negative* values of $\frac{dp}{dt}$; for Δb *positive,* on the other hand, *from* a point of inflection D,C to a critical point E,D, thus running *from below upward* always with *positive* values of $\frac{dp}{dt}$. For a definite value of Δb the two end-points of this curve, which is limited on both sides in this way, will coincide (and accordingly also the *three* points E, D, and C), and the whole coexistence-curve reduces to a single point (fig. 26).

We shall prove the above in the following paragraphs.

25. In the first place it may be observed that the equation of dissociation :

$$\frac{\beta^2}{1-\beta^2}=\frac{cT^{\prime+1}\, e^{-\frac{q_0}{RT}}\, e^{-\frac{(p+a/v^2)\Delta b}{RT}}}{p+a/v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

now gives rise to an altogether different shape of $\beta=f(v)$ for T constant. If Δb is negative, the course is as in fig. 21, with a minimum in M; for Δb positive the course is indicated by fig. 22. This is at once evident when $p+a/v^2$ is replaced by $\frac{(1+\beta)RT}{v-b}$ in the above equation, by which it becomes.

$$\frac{\beta^2}{1-\beta}={}^c/R\, T^{\prime}\, e^{-\frac{q_0}{RT}} e^{-\frac{(1+\beta)\Delta b}{v-b}}\,(v-b) \quad . \quad . \qquad (b)$$

For Δb negative the value of β will approach unity both for $v=b$ and for $v=\infty$; whereas for Δb positive for $v=b$ the value of β approaches zero on account of the exponential factor, which then becomes $e^{-\infty}$. The transition of β from 1 (liquid state) to near 0 (solid state) takes place in the *descending* portion AB for Δb negative (fig. 21); on the other hand the transition of β from 0 (solid state) to near 1 (liquid state) will take place in the *ascending* part AB for Δb positive (fig. 22). As we saw in the preceding papers, the increase of β from the minimum M to 1 again, takes place for Δb negative in the vapour phase and large values of v.

Now for Δb positive the change between A and B (fig. 22) will take place for small volumes only, when q_0 is not too large. For else evidently in consequence of the small value of the exponential factor $e^{-\frac{q_0}{RT}}$ — the index of which has now no longer the reversed sign of that of $-\frac{(p+a/v^2)\Delta b}{RT}$, but the same — the nearly asymptotic course of OA will continue to the neighbourhood of great values of v, and the change of β will take place between A and B in the *vapour phase*. But this evidently prevents the isotherm from twice taking a turn (in consequence of the rapid decrease of a/v^2 (from the value $\frac{a}{b_1^2}$ to the value $\frac{a}{(2\,b_2)^2}$) between the volumes $v=b_1$ (solid) and

$v = 2b_2$ (liquid), which gives rise to the coexistence solid-liquid. In other words there is no value of Δb for which a coexistence-curve solid-liquid will occur.

This is immediately seen, when we e. g. assume $q_0 = 3200$, as in our former example for Δb negative.

If we now namely put (equation I p. 773)

$$\frac{p + a/v^2}{RT}\Delta b = \varphi \quad ; \quad \frac{RT}{q_0} = \theta \quad ; \quad \frac{cq_0^{\gamma}}{R^{\gamma+1}}\Delta b = \lambda, \quad . \quad . \quad . \quad (c)$$

(a) passes into:

$$\frac{\beta^2}{1-\beta^2} = \lambda\theta^{3/2} e^{-1/\theta} \; \frac{e^{-\varphi}}{\varphi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

This agrees entirely with the preceding form, except that now $e^{-\varphi}$ occurs and not e^{φ}. With $\Delta b = 0{,}5$ and $T = 9$ (see I p. 774) we now find:

$$log^{10} \frac{\beta^2}{1-\beta^2} = -\,76{,}077 - 0{,}4343\,\varphi - log^{10}\,\varphi,$$

with the same values of a, b_1, c, and q_0 as in our preceding papers. In this equation $-\,0{,}4343\,\varphi$ occurs instead of $+\,0{,}4343\,\varphi$. But in consequence of this not before $\varphi = 10^{-74}$ the value of $log^{10} \frac{\beta^2}{1-\beta^2}$ will become such that β begins to move away from 0 (the point A in fig. 22), viz. $= -\,2{,}077$; while at $\varphi = 10^{-78}$ the value of log^{10} rises to 1,923, and β gets in the neighbourhood of 1 (the point B in the same figure). But in consequence of the formula $v = b + (v - b)$, i. e. $v = (b_1 + \beta\Delta b) + \frac{1+\beta}{\varphi}\Delta b$, or (cf. formula (5) on p. 773)

$$v = b_1 + \left(\beta + \frac{1+\beta}{\varphi}\right)\Delta b\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

v will then be of the order 10^{74}, resp. 10^{78}.

Even at $T = 100$, in consequence of which

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

the portion AB evidently lies between $\varphi = 10^{-2}$ and 10^{-6}, i. e. v between 50 and 10^6 (in the first case β is namely $= 0$, in the second $= 1$), so at much too large volumes.

Not before $T = 200$ the change of β from 0 to 1 would be found between values of v which might deserve consideration — but then we have already arrived above the critical temperature vapour-liquid, which lies at 133° for $\Delta b = 0{,}5$.

So we are obliged to lower the value of q_0 in such a way that the value of λ becomes considerably smaller. If e. g. we take q_0 a hundred times smaller than in our former example, i. e. $q_0 = 32$, we have the following values ($\Delta b = 0{,}5$):

$c = 2$, $q_0 = 32$ (both Gr. Cal.) $b_1 = 1$, $2b_2 = 1{,}5$, $a = 2700$.

The value of $2b_2 = b_1 + \Delta b$ (liquid) is now not $1 - 0{,}5 = 0{,}5$, but $1 + 0{,}5 = 1{,}5$, i. e. greater than that of b_1 (solid). The critical temperature (vapour-liquid) is found from:

$$(1+\beta)\, RT_c = \frac{8}{27}\frac{a}{2b_2},$$

assuming that for T_c all the double molecules are dissociated, hence b has become $= 2b_2$. This gives $(\beta=1)\; 4T_c = \frac{8}{27} \times \frac{2700}{1^1/_2} = \frac{1600}{3}$, so:

$$T_c = \frac{400}{3} = 133^1/_3 .$$

In our former example, where $\Delta b = -\,^1/_2$, and so $2b_2 = {}^1/_2$, T_c was $= 400°$.

The critical pressure now is $p_c = \frac{1}{27}\frac{a}{(2b_2)^2} = \frac{1}{27} \times \frac{2700}{2^1/_4} = \frac{400}{9} = 44^4/_9$, instead of 400 for $\Delta b = -0{,}5$.

26. Now we proceed to the more accurate calculation of the coexistence-curve solid-liquid for

$\underline{\Delta b = 0{,}5}$ ($b_1 = 1$, $2b_2 = 1{,}5$),

indicated in fig. 23.

The successive isotherms, belonging to the different points of the curve *PQSRCr* in fig. 23, are represented in the figures 27—32. In fig. 27 the stage below the point *P*, where coexistence vapour-solid is only possible (on the line *OS* of fig. 23). In fig. 28 the point of inflection *D,C* appears (*P* in fig. 23), and somewhat later (fig. 29) the first coexistence liquid-solid (the point *Q* in fig. 23). As this, however, takes place at negative pressures, the said coexistence is not realisable, and for the present only the coexistence vapour-solid is found as in fig. 27 and 28.

Only at still higher temperature (e. g. the point *R* in fig. 23) the coexistence liquid-solid has become realisable (and this already starting from the triple point *S*), which is represented in fig. 30. Now we have at first vapour-liquid, and at higher pressures liquid-solid. In fig. 31 the *critical point* liquid-solid (*Cr* in fig. 23) appears, after which (fig. 32) no coexistence liquid-solid is possible any more. Then only vapour-liquid remains — till at last this too disappears at the usual critical temperature (vapour-liquid).

Also in the figures 24, 25, and 26 these stages are passed through in quite the same succession; only everything is more compressed then, that is, the distance between the points P and Cr becomes smaller and smaller, and the coexistence-curve will at last quite disappear from the field (fig. 26).

Let us now calculate $\underline{T=50}$ for $\Delta b=0{,}5$ (fig. 28). The value of λ (cf. the formula (c)) is $=32$. Further θ is $=\frac{25}{8}$, so that (d) passes into

$$log^{10}\frac{\beta^3}{1-\beta^2}=2{,}109-0{,}4343\varphi-log^{10}\varphi.$$

Then the values of v are calculated from (e), i. e.:

$$v=1+0{,}5\left(\beta+\frac{1+\beta}{\varphi}\right),$$

and those of p from (compare (4) on p. 773 loc. cit.):

$$p=\frac{RT}{\Delta b}\varphi-\frac{a}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

i. e. here from

$$p=200\varphi-\frac{2700}{v^2}.$$

This gives the following survey.

$T=50$

φ	log^{10}	β	v	$^a/_{v^2}$	p
8	4.377	0 073	1.104	2217	—617
7	3.885	0.128	1.145	2029	—629
6	3.384	0.225	1.214	1832	—632 (E)
5	2.871	0 384	1.330	1526	—526
4	2.339	0.609	1.505	1192	—392
3	1.780	0.825	1.717	916	—316
2	1.170	0.947	1.960	703	—303
1	0.434	0.990	2.490	435	—235

So the temperature of the point of inflection D,C lies somewhat above 50°, viz. at $\underline{T=52{,}3}$ ($p_{D,C}=-282$).

For $\underline{T=60,}$ for which $\theta=\frac{15}{4}$,

$$log^{10}\frac{\beta^2}{1-\beta^2}=2{,}250-0{,}4343\varphi-log^{10}\varphi \quad ; \quad p=240\varphi-\frac{2700}{v^2},$$

holds, from which we calculate:

$T = 60$

φ	log^{10}	β	v	$^a/_{v^2}$	p
8	—2.127	0 086	1 111	2188	—268
7	—1 635	0.150	1 157	2016	—336 (*E*)
6	—1 134	0.262	1.236	1767	—327
5	—0.621	0 440	1 364	1451	—251
4	—0 089	0.670	1.544	1133	—173
3	+0.470	0.864	1.743	889	—169 (*D*)
2	1.080	0 961	1.971	695	—215 (*C*)
1	1.816	0.992	2.492	435	—195

A maximum has appeared at D and a minimum at C, but no coexistence pressure as yet, because the pressure-curve about halfway E and D ($p = \pm - 250$) still runs below C. (Fig. 29).

So let us repeat the calculation for $T = 65$. Here $\theta = \frac{65}{16}$, and with

$$log^{10} \frac{\beta^2 l}{1-\beta^2} = 2{,}311 - 0{,}4344\varphi - log^{10}\varphi \quad ; \quad p = 260\varphi - \frac{2700}{v^2}$$

we get the following survey :

$T = 65$

φ	log^{10}	β	v	$^a/_{v^2}$	p
7	—1.574	0.161	1.164	1992	—172
6	—1.073	0.279	1.246	1739	—179 (*E*)
5	—0.560	0.465	1.379	1419	—119
4	—0.028	0 696	1 560	1110	— 70 (*D*)
3	+0.531	0.879	1.752	879	— 99
2	1.141	0.966	1.974	693	—173
1	1 877	0.993	2.493	435	—175 (*C*)
0.5	2.395	0 998	3.497	221	— 91

The coexistence-pressure liquid-solid is about -125; and it is real, because now -125 is greater than the pressure in C. Hence the case of fig. 29 lies between 60° and 65°. By interpolation we easily calculate that the pressure of coexistence (fig. 29) first makes its appearance at 62°, where then $p = p_C$ is about $= -200$.

Now this pressure is real, but still unrealisable as negative pressure.

Now we calculate the isotherm of $T = 70$. Here $\theta = \frac{35}{8}$, and further:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}367 - 0{,}4343\varphi - log^{10}\varphi \quad ; \quad p = 280\varphi - \frac{2700}{v^2},$$

from which the following table is drawn up.

$T = 70$

φ	log^{10}	β	v	a/v^2	p
7	—1.518	0 172	1.170	1972	— 12
6	—1 017	0.296	1 256	1711	— 31 *(E)*
5	—0 504	0.488	1.393	1392	+ 8
4	+0.020	0.718	1.574	1090	+ 30 *(D)*
3	0 587	0 891	1 761	871	— 31
2	1.197	0 970	1.977	691	—131
1	1.933	0 994	2.494	434	—154 *(C)*
0.5	2.451	0.998	3.497	221	— 81

The pressure of coexistence liquid-solid is about $p = 0$, so that we have reached the triple point S (fig. 23), and from this moment the mentioned pressure becomes realisable.

Now $T = 75$ (fig. 30) must be calculated for the determination of the point Cr (fig. 23). With $\theta = \frac{75}{16}$ we get:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}419 - 0{,}4343\varphi - log^{10}\varphi \quad ; \quad p = 300\varphi - \frac{2700}{v^2}.$$

This yields:

$T = 75$

φ	log^{10}	β	v	a/v^2	p
7	—1.466	0.182	1.175	1955	145
6	—0.965	0 313	1.266	1684	116 *(E)*
5	—0 452	0.511	1 406	1366	134 *(D)*
4	+0 080	0.739	1.587	1072	128
3	0 639	0.902	1.768	864	36
2	1.249	0 973	1 979	689	— 89
1	1.985	0.995	2 495	434	—134 *(C)*
0.5	2.503	0.998	3.497	221	— 71

So the coincidence of E and D in a *critical point* solid-liquid will take place somewhat above 75°.

Finally we calculate $T=80$ (fig 31) for this purpose. Then $\theta=5$ and

$$log^{10}\frac{\beta^2}{1-\beta^2}=2,467-0,4343\varphi-log^{10}\varphi \quad ; \quad p=320\varphi-\frac{2700}{v^2},$$

which gives rise to the following table.

$T=80$

φ	log^{10}	β	v	a/v^2	p
7	—1.418	0 192	1.181	1935	305
6	—0 917	0.229	1.275	1661	259 } E,D
5	—0.404	0 532	1 419	1341	259 }
4	+0.128	0.757	1 598	1057	223
3	0.687	0.911	1 774	858	102
2	1 297	0.976	1.982	687	— 47
1	2 033	0.995	2 495	434	—114 C
0 5	2.551	0 998	3.497	221	— 61

So the coincidence takes place at exactly 80°.

If we now examine the foregoing tables, it appears (see fig. 23), that the whole curve of coexistence solid-liquid extends from $T=62$, $p=-200$ (the point Q) to $T=80$, $p=259$ (the point Cr). Only the part above S, ($T=70$), $p=0$), however, is realisable.

The triple-point S lying at 70°, and the critical temperature vapour-liquid being $=133°$, we have here:

$$\frac{T_0}{T_c}=\frac{70}{133}=0,53,$$

which is in perfect harmony with the value which was found for it in many cases.

We remind the reader that for this relation (provided T_0 does not lie too near any critical point) the general equation [see V, p. 461, formula (27a)]

$$\frac{T'_0}{T_c}=\frac{27}{8}\left(\frac{-\Delta b}{b_1}\right)^2 : log\left(\frac{b_1^2}{4b_2^2}\cdot\frac{1}{2\beta'}\right)$$

holds.

With $\Delta b=0,5$, $b_1=1$, $b_2=1,5$ this becomes:

$$\frac{T_0}{T_c}=\frac{27}{32} : log\left(\frac{2}{9\beta'}\right)$$

For this we find the value 0,5, when $\frac{2}{9\beta'} = 5{,}5$, i.e. $\beta' = 0{,}04$, which is a very plausible value.

When the value of Δb diminishes, also the value of $T_0 : T_c$ becomes slightly less, but remains in the neighbourhood of 0,5. But as we shall immediately see, the whole of the coexistence-curve liquid-solid has come below $p = 0$, already for $\Delta b = 0{,}4$, and so it is no longer realisable — at least with the values of b_1, Δb, etc. assumed by us.

This will appear from the tables following here, which hold for $\Delta b = 0{,}4$.

27. We shall calculate the isotherms of 50°, 60°, and 70° for the case (see fig. 24)

$$\underline{\Delta b = 0{,}4} \ (b_1 = 1,\ 2b_2 = 1{,}4).$$

The value of λ is then $= 25{,}6$. The critical data are $T_c = 143°$, $p_c = 51$ (cf. § 25; $2b_2$ is then namely $= 1{,}4$).

For $\underline{T = 50}$ we have $\theta = \frac{25}{8}$, and the formula (d) passes into

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}012 - 0{,}4343\ \varphi - log^{10}\ \varphi,$$

while

$$v = 1 + 0{,}4\left(\beta + \frac{1+\beta}{\varphi}\right) \quad ; \quad p = 250\ \varphi - \frac{2700}{v^2}.$$

In consequence of this we get:

$T = 50$

φ	log^{10}	β	v	a/v^2	p
7	—1 873	0.115	1.110	2193	—443
6	—1.372	0 202	1 161	20 4	—504 (E)
5	—0 859	0.348	1.247	1735	—485
4	—0.327	0 566	1.383	1412	—412
3	+0.232	0.794	1 557	1114	—364 (D)
2	0 842	0.935	1.761	871	—371 (C)
1	1 578	0 987	2.190	563	—313

For $\underline{T = 60}$ we have $\theta = \frac{15}{4}$, and further:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2,154 - 0,4343\, \varphi - log^{10} \varphi \quad ; \quad p = 300\, \varphi - \frac{2700}{v^2},$$

from which we calculate:

$T = 60$

φ	log^{10}	β	v	a/v^2	p
7	—1 731	0.135	1.119	2156	— 56
6	—1.230	0.236	1 177	1951	—151
5	—0.717	0.401	1 273	1668	—168 *(E)*
4	—0 185	0.628	1.414	1350	—150 *(D)*
3	+0 374	0.838	1 580	1081	—181
2	0.984	0.952	1.771	861	—261
1	1.720	0.991	2.193	562	—262 *(C)*
0.5	2.238	0.997	2.996	301	—151

So the coincidence D,C lies just before 50°, and the first appearance of the pressure of coexistence between 50° and 60°. By interpolation we find easily the value $T = 49$ ($p = -382$) for the point P (cf. fig. 28), and the value $T = 54$ ($p = p_C = -327$) for the point Q (comp. also fig. 29).

Now we have still to calculate $T = 70$ for the calculation of the point Cr. For this $\theta = \frac{35}{8}$, and we have:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2,271 - 0,4343\, \varphi - log^{10} \varphi \quad ; \quad p = 350\, \varphi - \frac{2700}{v^2},$$

which gives rise to the following table.

$T = 70$

φ	log^{10}	β	v	a/v^2	p
7	—1 614	0.154	1.128	2123	+327
6	—1.113	0.267	1.191	1903	+197
5	—0 600	0.448	1.295	1610	+140
4	—0.068	0.679	1.439	1303	+ 97
3	+0 491	0.869	1.597	1059	— 9
2	1 101	0.963	1.778	855	—155
1	1.837	0.993	2.194	561	—211 *(C)*
0.5	.2 355	0.998	2.998	300	—125

So in this case (compare fig. 32) we are far beyond the coincidence E,D. But by interpolation between 60° and 70° we find for $T=63$:

$$
\begin{array}{rrrrrrrr}
{}^{a}/_{v^2} = & 2146 & 1937 & 1651 & 1336 & 1074 & 859 & 562 \\
315\,\varphi = & 2205 & 1890 & 1575 & 1260 & 945 & 630 & 315 \\
\hline
p = & 59 & -47 & \underbrace{-76 \quad -76}_{E,D} & & -129 & -229 & \underset{C}{-247}
\end{array}
$$

so that the said coincidence takes place at $\underline{T=63}$ ($p_{E,D}=-76$).

So we see that the whole coexistence-curve solid-liquid falls in the region of negative pressures, from $T=54$, $p=-327$ to $T=63$, $p=-76$. Accordingly the coexistence-curve vapour-liquid OK is *not* intersected by that for solid-liquid, and there exists *no solid state.*

If for $\Delta b=0{,}5$ the line QCr extended from 62° to 80°, i.e. over a region of 18°, now it has contracted for $\Delta b=0{,}4$ to a region of only 9°, viz. from 54° to 63°.

28. Let us now calculate the case (see fig. 25)

$$\underline{\Delta b=0{,}3} \quad (b_1=1,\ 2b_2=1{,}3)$$

The whole curve lies between 40° and 50°, and so we determine the values of p for these two temperatures. The value of λ is now $=19{,}2$; further $T_c=154$, $p_c=59$.

For $\underline{T=40}$ we have $\theta={}^5/_2$, and therefore:

$$\left.\begin{array}{l} log^{10}\dfrac{\beta^2}{1-\beta^2}=1{,}706-0{,}4343\,\varphi-log^{10}\,\varphi \\[2ex] v=1+0{,}3\left(\beta+\dfrac{1+\beta}{\varphi}\right); \qquad p=266{,}7\,\varphi-\dfrac{2700}{v^2}\end{array}\right\}$$

From this we find:

$T=40$

φ	log^{10}	β	v	${}^a/_{v^2}$	p
6	−1.678	0.143	1.100	2231	−631
5	−1.165	0.253	1.151	2038	−705 *(E)*
4	−0.663	0.435	1.238	1761	−694
3	−0.074	0.677	1.371	1436	−636
2	+0.556	0.880	1.546	1130	−597
1	1.272	0.974	1.884	761	−494

For $\underline{T=50}$ we have $\theta=\dfrac{25}{8}$, and further:

$$log^{10}\frac{\beta^2}{1-\beta^2}=1{,}887-0{,}4343\,\varphi-log^{10}\,\varphi\ ;\ p=333{,}3\,\varphi-\frac{2700}{v^2},$$

from which the following table can be drawn up.

$T = 50$

φ	log^{10}	β	v	$a/_{v^2}$	p
6	—1.497	0.176	1.112	2183	—183
5	—0.984	0.306	1.170	1982	—305
4	—0.452	0.511	1.267	1683	—350 }
3	+0.107	0.749	1.400	1378	—378 }
2	0.717	0.916	1.562	1107	—140 *(C)*
1	1.453	0.983	1.890	756	—123

For 40° (cf. fig. 27) the point of inflection D,C (fig. 28) has not yet been reached; for 50° (fig. 32) we are already far beyond the coincidence E,D (fig. 31).

Now we find by interpolation:

$T = 44$

$$p = 293{,}3\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p
6	2212	—452
5	2012	—545
4	1730	—557 *(E)*
3	1413	—533 } *D,C*
2	1121	—534 }
1	759	—466

$T = 45$

$$p = 300\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p
6	2207	—407
5	2005	—505
4	1722	—522 *(E)*
3	1407	—507 *(D)*
2	1119	—519 *(C)*
1	758	—459

$T = 46$

$$p = 306{,}7\,\varphi - \frac{2700}{v^2}$$

φ	$a/_{v^2}$	p
6	2202	—362
5	1998	—465
4	1714	—487 *(E)*
3	1401	—481 *(D)*
2	1116	—503 *(C)*
1	758	—451

$T = 47$

$$p = 313{,}3\,\varphi - \frac{2700}{v^2}$$

φ	$a/_{v^2}$	p
6	2197	—317
5	1992	—425
4	1706	—453 }
3	1395	—455 }
2	1114	—487 *(C)*
1	757	—444

42*

It appears from these tables that the coincidence D,C now takes place at $\underline{T=44}$ ($p_{D,C}=-534$). Further that the first pressure of coexistence liquid-solid (fig. 29) appears at $\underline{T=44{,}7}$ ($p=p_C=-524$).

For then we have with $p=298\varphi-\frac{2700}{v^2}$, resp. for $\varphi=4$, 3 and 2:

$^a/_{v^2}=$	1724,4	1408,8	1119,6
$p=$	$-532{,}4$	$-514{,}8$	$-523{,}6$
	E	D	C

so that the pressure of coexistence is about 523,6, p_C also having this value.

Finally it appears that the coincidence E,D takes place at $\underline{T=46{,}7}$ ($p_{E,D}=-463$). For then we have resp. for $\varphi=4$ and 3:

$$^a/_{v^2}=1708{,}4 \text{ and } 1396{,}8 \quad ; \quad p=463{,}1 \text{ and } 462{,}8.$$

So in the case $\Delta b=0{,}3$ the whole coexistence-curve only stretches over an interval of 2° viz. from 44°,7 to 46°,7, again in the region of negative pressures, hence not realisable.

29. It is now easy to derive that the coexistence-curve entirely disappears from the field for

$$\underline{\Delta b=0{,}276} \quad (T_c=157,\ p_c=61).$$

Then for

$$\underline{T=43}, \quad \underline{p=-570}$$

the end-points P and Cr coincide, and in the isotherm of 43° the points E, D, and C coincide to a contact of higher order.

For $\Delta b=0{,}4$ the difference of temperature between the end-points P and Cr amounts to 14°, whereas this is only 2°,7 for $\Delta b=0{,}3$. By interpolation we find from this that the difference 2°,7 has been reduced to 0 for $\Delta b=0{,}3-0{,}24\,(0{,}4-0{,}3)$, i.e. for 0,276. Then $T_{D,C}=T_{E,D,C}=44-0{,}24\times5=42{,}8$, while $p_{D,C}=p_{E,D,C}=$ $=-534-0{,}24\times152=-570$.

If we finally comprise everything found for Δb positive in one table, we get the following summary.

$\Delta b=0.5$	0.4	0.3	0 276
$T_P=52.3$ ($p=-282$)	49 (—382)	44 (—534)	
$T_Q=62$ ($p=-200$)	54 (—327)	44.7 (—524)	42.8 (—570)
$T_{Cr}=80$ ($p=+259$)	63 (— 76)	46.7 (—463)	

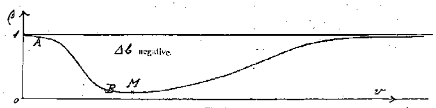

Fig. 21.

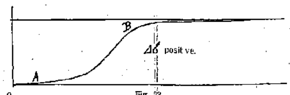

Fig. 22.

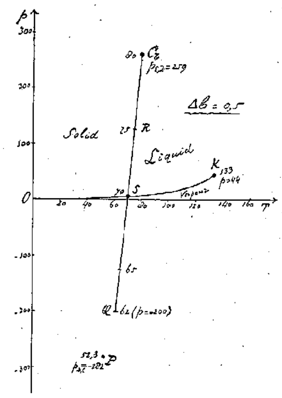

Fig. 23.

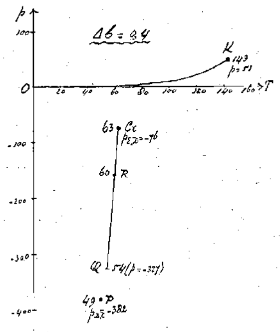

Fig. 24.

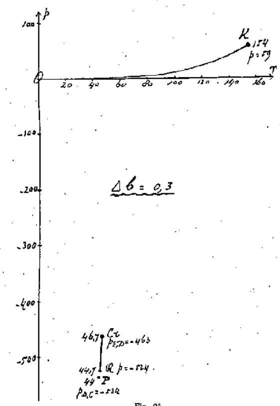

Fig. 25.

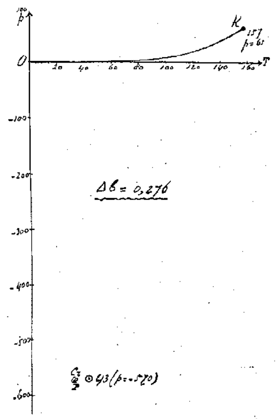

Fig. 26.

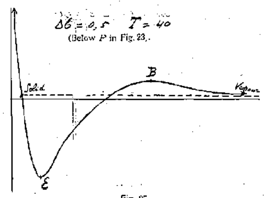

Fig. 27

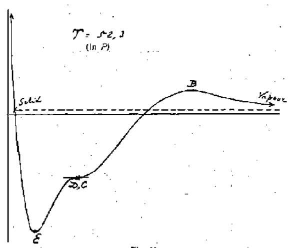

Fig. 28.

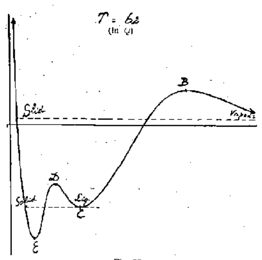

Fig. 29.

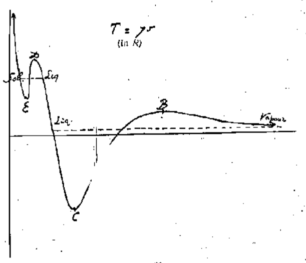

Fig. 30.

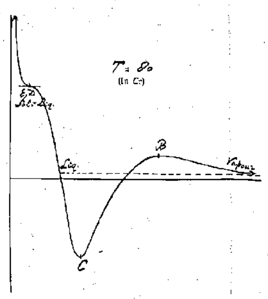

Fig. 31

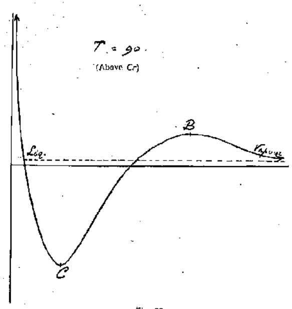

Fig. 32.

So just as for Δb negative (see our preceding paper) we have a realisable coexistence-curve liquid-solid, viz. with *positive* pressures above a *triple-point* S, for Δb positive only when Δb has a sufficiently high value (here $= 0{,}5$). For Δb positive this triple-point lies at about $^1/_2\, T_c$, in accordance with what was found experimentally for many substances.

In how far these results are still subject to modification, when not — as was supposed up to now — *two* simple molecules associate to one complex molecule, but more than two, we shall have to discuss in a concluding paper. Moreover some remarks will be made about some papers by VON WEIMARN, who lately also concluded to the improbability of the TAMMANN melting-point curve on the ground of crystallographic-molecular considerations, and who then already stated the *probable* existence of a critical point solid-liquid, which existence, however, has only been raised beyond doubt by our theoretical considerations.

Physiology. — *"On the negative variation of the nervus acusticus caused by a sound."* By F. J. J. BUIJTENDIJK. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of November 26, 1910).

Up till now of the electric phenomena caused by the natural irritation of the organs, only those of the retina and of the nervus opticus have been investigated. [1]).

As I have been told, about 1904 a French investigator observed electric currents with a mirror galvanometer, when he connected this measuring apparatus with the nervus acusticus of a rabbit and a loud sound struck the ear of the experimental animal.

With the string-galvanometer of EINTHOVEN I succeeded in registrating the action-currents of the nervus acusticus suggested by a natural irritation. Under ether-narcosis of the experimental animal, electrodes of a specific form were placed by means of a trepanation opening into the hindmost skull-cavity of a cavia. These electrodes, a thin metallic tube, containing an isolated metallic pin were pushed on along the side-parietes of the cerebellum, usually after piercing the juncture of the flocculus with the rest of the cerebellum. In this way a trial was made to reach the nervus acusticus with the extremity

1) Vide a. o. EINTHOVEN and JOLLY. Quart. Journal of Experim. Physiol. Volume I. 1908 page 373.