Citation:

J.J. van Laar, On the course of the plaitpoint line and of the spinodal lines also for the case that the mutual attraction of the molecules of one of the components of a binary mixtures of normal substances is slight, in:
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and 18° C. in malt extract and transferring to boiled milk or whey at a somewhat higher temperature. The acidity obtained remains low and amounts to 3 to 5 c.c. of normal acid per 100 c.c. of milk.

The elective culture of *Lactococcus* takes place by allowing milk to sour in a stoppered bottle at 20° to 25° C. and transfer it repeatedly to boiled milk at that temperature. The thereby obtained stocks of *Lactococcus lactis* are mostly anaërobic but specifically not to be distinguished from the more aërobic forms which may be produced by the same experiment. The acid mostly remains at about 8 c.c. of normal acid per 100 c.c. of milk, but may become 10 to 12 c.c.

The elective culture of *Lactobacillus* succeeds best by cultivating buttermilk in absence of air at 37° to 40° C. and inoculating it into boiled milk, at 30° C. and higher, the acidity can rise from 18 to 25 c.c. of normal acid per 100 c.c. of milk.

The active lactic acid ferments are very variable; as factors of hereditary constant variation are recognised cultivation at too high or too low oxygen pressure, and cultivation at a temperature above the optimum of growth.

Lactic acid ferments do not lack in the intestinal flora, but play there an inferior part.

A considerable difference between Eastern and Western lactic acid ferments does not exist.

Yoghurt and other such like sour milk preparations deserve the attention of hygienists.

Chemistry. — *"On the course of the plaitpoint line and of the spinodal lines, also for the case, that the mutual attraction of the molecules of one of the components of a binary mixture of normal substances is slight"*, by Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 26, 1907).

1. In the latest volume of These Proceedings [1]) Dr. KEESOM (also in conjunction with Prof. KAMERLINGH ONNES) stated some important results, inter alia concerning his investigation on the special case that one, e.g. a_1, of the two quantities a_1 and a_2 is very small; which is

[1]) KAMERLINGH ONNES and KEESOM, These Proc., Dec. 29, 1906, p. 501—508 [On the gas phase sinking in the liquid phase etc. (Comm. 96*b*)]; KEESOM, Ibid. p. 508—511 [On the conditions for the sinking etc. (Comm. 96*c*)]; KEESOM, Ibid. March 28, 1907, p. 660—664 (Comm. 96*c* continued); KAMERLINGH ONNES and KEESOM, Ibid. of April 25, 1907, p. 786—798 [The case that one component is a gas without cohesion etc. (Suppl. N°. 15)].

realised, among others, for mixtures of He (a_1) and H_2 (a_2). In these papers, particularly in the last, a particular kind of plaitpoint line has been repeatedly mentioned, viz. one passing from the critical temperature T_0, called "third" by me (KEESOM's T_{km}), to the *highest* of the two critical temperatures T_2 (KEESOM's T_{k_1}).

Now the theoretical possibility of such a course of the plaitpoint line, i.e. *of one of its two branches*, has been first brought to light by me in a series of Discussions on this subject [1]. Not only for the special case $b_1 = b_2$, for which among others, fig. 1 of June 21, 1905 holds, but for all possible cases (see specially TEYLER I and II). We found that such a course will always be found, when the ratio of the two critical temperatures $\theta = \frac{T_2}{T_1}$ is *larger* than the value of this ratio, for which the plaitpoint line has a *double point*. This type was called type I by me. (see also fig. 1 of Oct. 25, 1906).

The case that a plait *starts* from C_0 to C_2, or also at the same time from C_2 to C_0 (when there is a minimum temperature in the plaitpoint line) is not new (see K. O. and KEESOM, p. 788 below), but has been before described and calculated by me in all particulars.

The *double point* in the plaitpoint line, discovered by me in 1905 (June 21), did not only give the key to the possibility of such a course, which had already been ascertained for mixtures of water and ether, of ethane and methylalcohol [2]; but also the *connection*

[1]) These Proc. May 25, 1905, p. 646—657; Ibid. June 21, 1905, p. 33—48; Ibid. Aug 17, 1905, p. 144—152 (Cf. also Arch. Néerl. 1905, p. 373—413); Ibid. Jan 25, 1906, p. 578—590 (Also Arch. Neerl. 1906, p. 224—238); Ibid. Oct. 25, 1906, p. 226—235. Further Arch. TEYLER (2) X, Première partie, p. 1—26 (1905); Ibid. Deuxième partie, p. 1—54 (1906). Henceforth I shall refer to papers in these Proceedings by mentioning the *date*, to papers in the Arch. TEYLER by putting TEYLER I or II.

[2]) I do not quite understand why in cases as for $He + H_2$ the plait considered is particularly called a *"gasplait"*. With exactly the same right the two coexisting phases might be called *liquid* phases, expecially at the higher pressures in the neighbourhood of the point C_0. With reference to water-ether, etc. we speak of a gas phase and a liquid phase before the three phase equilibrium is reached, i. e. at higher temperatures; and when at lower temperatures the equilibrium mentioned has established itself, of two liquid phases. The "gas phase" is then determined by the branch plait of the original transverse plait (which latter has now the peculiar shape directed towards C_0 in the neighbourhood of the axis $x = 0$. But I acknowledge that this is perfectly arbitrary, it being difficult to indicate where the pressure is high enough on such a plait to justify us in speaking of liquid phases. Would it not be better to follow here VAN DER WAALS' terminology, and speak of *fluid* phases, and to call the two phases *liquid* phases at temperatures where the three phase equilibrium is found? Otherwise in this latter case — keeping to K. O. and KEESOM's terminology — we should have to speak of *three* coexisting *gas phases*, a rarefied one and two very dense ones, which latter, however, we should never refer to as gas phases in the *perfectly identical* case of water + ether.

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of the different series of *hidden* plaitpoints, etc. etc., as has, inter alia, been indicated in Jan. 25, 1906 (cf. also TEYLER II). Dr. KEESOM does not mention that in his figure I (loc. cit. p. 794) besides the plaitpoint line from K_m to K_1 drawn there, there *always* exists also a *second* branch, which runs along the v-axis in the neighbourhood of $x=1$ from the point where $v=b$ to K_2 — and which gives rise to a *three phase equilibrium* at lower temperatures, as this has been explained by me. (also in Jan. 25, 1906 and TEYLER II).

The fact whether a plait extends in the way mentioned, depends therefore, as we said before, *in the first place* on the fact whether the values of $\frac{b_2}{b_1}$ and $\frac{a_2}{a_1}\left(\text{so of } \theta=\frac{T_2}{T_1} \text{ and } \pi=\frac{p_2}{p_1}\right)$ are such that θ is larger than that value of θ for which the plaitpoint line has a *double point* with given value of π. The knowledge of this double point, being therefore of so great importance for the distinction of the different types, I have carried out in TEYLER I the lengthy calculations required for this, and drawn up the results obtained in tables. [See also TEYLER II, where fig. 22 (p. 30) represents the results *graphically*].

Hence *not* the fact that $T_{km} > T_{k_1}$ [with perfect justice KEESOM says in a footnote (loc. cit. p. 794) that T_{km} may also be $< T_{k_1}$], but only the fact that θ lies *above the double point value,* determines the considered course of the plaitpoint line. (See also Oct. 25, 1906, where I summed up most of the results obtained by me).[1])

It is true that KEESOM mentions in a note (loc. cit. p. 786) that I have examined the plaitpoint line for the case $a_1=0$, but this statement is not quite complete, for I have not only examined such a plaitpoint line for this particular case $a_1=0$, which I cursorily mentioned in a note (June 21, 1905, p. 39), but for all cases. Qualitatively the plaitpoint line $C_0\ C_2$ for the case $a_1=0$ is not distinguished in anything from that for the case $a_1>0$ (provided it remain in the case of type I), hence there was no call for a special investigation of the form of the spinodal line and of the plait for $a_1=0$, this having already been done for the general case. Moreover KEESOM himself considers later on the case a_1 *small,* and no longer $a_1=0$, which of course does not occur in practice.

Also the equation of the spinodal line (for molecular quantities):

$$RTv^3 = 2\,(1-x)\,(v\sqrt{a_1} - b_1\sqrt{a})^2 + 2x\,(v\sqrt{a_2} - b_2\sqrt{a})^2,$$

1) Prof. VAN DER WAALS says (These Proc., March 28, 1907, p. 621), "that as yet no one has succeeded in giving a satisfactory explanation of the different forms (of plaits)." I think I have done so to a certain degree in my papers of 1905--1906.

given by KEESOM, had already been drawn up by me (May 25, 1905, p. 652) in the identical form:

$$RTv^3 = 2\left[x(1-x)(av - \beta\sqrt{a})^2 + a(v-b)^2\right],$$

where $\alpha = \sqrt{a_2} - \sqrt{a_1}$ and $\beta = b_2 - b_1$.

2. The answer to the question whether the plait extends from C_0 to C_2 *with* or *without* double point in the *spinodal* curve, i. e. with or without *minimum* plaitpoint temperature, in other words the answer to the question whether the plait passes from C_0 to C_2 undivided, or whether two plaits extend on the ψ-surface, one starting from C_0, the other from C_2, which meet at the minimum temperature — depends on the value of $\theta = \frac{T_2}{T_1}$ (on which also $\frac{T_2}{T_0}$ depends) for given value of $\pi = \frac{p_2}{p_1}$. The condition for this I derived in Aug. 17, 1905, p. 150, and Jan. 25, 1906, p. 581. In the summer of 1906 I calculated the place of the minimum itself (Cf. Oct. 25, 1906, 234, line 18—16 from the bottom), but seeing that the paper, which at that time had already been completed and sent to the editor of the Arch. Teyler, has not yet been published (it may be even some time before it is), I think it desirable to publish already now the calculation in question.

Like the calculations of KEESOM, VERSCHAFFELT and others, it starts from the supposition that a and b do not depend on v or T, and that these quantities may be represented by

$$a_x = [(1-x)\sqrt{a_1} + x\sqrt{a_1}]^2 \quad ; \quad b_x = (1-x)\,b_1 + x\,b_2 .$$

So in conformity with BERTHELOT and others we assume that $a_{12} = \sqrt{a_1 a_2}$. Some time ago Prof. VAN DER WAALS raised his voice against this supposition [1]), and it seems to me that there is really much to be said in favour of a_{12} being *in general not* $= \sqrt{a_1 a_2}$. But as a first approximation the equation put may be accepted, the more so as also the variability of b with v and T is neglected. That in consequence of the assumption $a_{12} = \sqrt{a_1 a_2}$ the left region, mentioned by VAN DER WAALS, would be compressed to an exceedingly small region, can hardly be adduced as an argument against this supposition; rather the fact that the attractions are *specific* quantities, and that therefore ε_{12} need not be $= \sqrt{\varepsilon_1 \varepsilon_2}$.

For the calculation of the minimum we start from the equation of the spinodal curve, derived by us (loc. cit.):

[1]) These Proc., March 28, 1907, p. 630—631.

$$RT = \frac{2}{v^3}\left[x(1-x)(av - \beta \sqrt{a})^2 + a(v-b)^2\right], \quad . \quad . \quad . \quad (1)$$

or

$$RT = \frac{2\alpha^2}{v}\left[x(1-x)\left(1 - \frac{\beta}{v}\frac{\sqrt{a}}{\alpha}\right)^2 + \frac{a}{\alpha^2}\left(1 - \frac{b}{v}\right)^2\right],$$

which with $\frac{b_1}{v} = \omega$, $\frac{\beta}{v} = n\omega$, $\frac{\sqrt{a_1}}{\alpha} = \varphi$ passes into

$$RT = \frac{2\alpha^2}{\beta} n\omega \left[x(1-x)\left(1 - n\omega(\varphi + x)\right)^2 + (\varphi + x)^2\left(1 - (1 + nx)\omega\right)^2\right]. (1a)$$

For $\frac{\sqrt{a}}{\alpha} = \frac{\sqrt{a_1} + x\alpha}{\alpha} = \varphi + x$ and $\frac{b}{v} = \frac{b_1 + x\beta}{v} = \omega + xn\omega = (1 + nx\omega)$.

Now the spinodal curve must show a double point, in other words:

$$\frac{\partial f}{\partial x} = 0 \quad \text{and} \quad \frac{\partial f}{\partial \omega} = 0,$$

when f represents the second member of (1a). The first equation gives:

$$(1-2x)(1-z)^2 - 2x(1-x)(1-z)n\omega + 2(\varphi + x)(1-y)^2 - 2(\varphi + x)^2(1-y)n\omega = 0,$$

when for the sake of brevity $n\omega(\varphi + x) = z$ and $(1 + nx)\omega = y$ is put. Bearing in mind that $n\omega = \frac{z}{\varphi + x}$, we get for the last equation:

$$(1-2x)(1-z)^2 - \frac{2x(1-x)}{\varphi + x}z(1-z) + 2(\varphi + x)(1-y)^2 - 2(\varphi + x)(1-y)z = 0. \quad (a)$$

The second equation yields, when in (1a) the factor ω is brought within [ ]:

$$x(1-x)\left[(1-z)^2 - 2\omega\ (1-z)n(\varphi + x\right] +$$
$$+ (\varphi + x)^2\left[(1-y)^2 - 2\omega(1-y)(1 + nx)\right] = 0,$$

or

$$x(1-x)\left[(1-z)^2 - 2z(1-z)\right] + (\varphi + x)^2\left[(1-y)^2 - 2y\ (1-y)\right] = 0,$$

i. e.

$$x(1-x)(1-z)(1-3z) + (\varphi + x)^2(1-y)(1-3y) = 0. \quad . \quad . \quad . \quad (b)$$

From (b) we solve:

$$x(1-x) = -(\varphi + x)^2\frac{(1-y)(1-3y)}{(1-z)(1-3z)}. \quad . \quad . \quad . \quad . \quad (\beta)$$

Also from (a):

$$= \left[-2(\varphi + x)(1-y)^2 + 2(\varphi + x)(1-y)z + \frac{2x(1-x}{\varphi + x}z(1-z)\right] : (1-z)^2,$$

or

$$1\text{-}2x = \left[-2(\varphi+x)(1\text{-}y)^2 + 2(\varphi+x(1\text{-}y)z - \frac{2(\varphi+x)(1-y)(1\text{-}3y)z}{1\text{-}3z)}\right] : (1\text{-}z)^2,$$

when for $x(1-x)$ the value from β is substituted. Further reduction yields:

$$1 - 2x = \left[-2(\varphi+x)(1-y)^2 + 2(\varphi+x)(1-y)z\left\{1 - \frac{1-3y}{1-3z}\right\}\right] : (1-z)^2,$$

or

$$1 - 2x = -\frac{2(\varphi+x)(1-y)}{(1-z)^2}\left[(1-y-3z\frac{y-z}{1-3z}\right],$$

or

$$1 - 2x = -\frac{2(\varphi+x)(1-y)}{(1-z)^2} \cdot \frac{(1-y)-3z(1-z)}{1-3z}. \quad . \quad . \quad (\alpha)$$

From (α) and (β) follows, as $(1-2x)^2 = 1 - 4x(1-x)$:

$$1 + 4(\varphi+x)^2\frac{(1-y)(1-3y)}{(1-z)(1-3z)} = \frac{4(\varphi+x)^2(1-y)^2}{(1-z)^4} \cdot \frac{\left[(1-y)-3z(1-z\right]^2}{(1-3z)^2},$$

i. e.

$$1 = \frac{4(\varphi+x)^2(1-y)}{(1-z)^4(1-3z)^2}\left[(1-y)\left\{(1-y)-3z(1-z)\right\}^2 - (1-3y)(1-z)^3(1-3z)\right].$$

Arrangement according to the powers of z yields for [ ]:

$$(3y^2-y^3) - 6z(y+y^2) + 3z^2(1+5y+2y^2) + z^3(-8-12y) + 6z^4,$$

or

$$y^2(3-y) - 6yz(1+y) + 3z^2(1+5y+2y^2) - 4z^3(2+3y) + 6z^4,$$

which may be reduced to

$$(y-z)^2(6z^2-8z+3-y),$$

so that we find:

$$1 = \frac{4(\varphi+x)^2(1-y)(y-z)^2(6z^2-8z+3-y)}{(1-z)^4(1-3z)^2},$$

from which may be solved:

$$(\varphi+x)^2_m = \frac{(1-z)^4(1-3z)^2}{4(1-y)(y-z)^2(6z^2-8z+3-y)}, \quad . \quad . \quad . \quad (2)$$

through which $\varphi + x$ is expressed in the two parameters y and z. In consequence of this (β) passes into

$$x_m(1-x_m) = -\frac{(1-z)^3(1-3z)(1-3y)}{4(y-z)^2(6z^2-8z+3-y)}, \quad . \quad . \quad . \quad . \quad (3)$$

from which x_m may be calculated with given values of y and z Then φ_m is also known through (2), i.e. expressed in y and z.

Further we now find for RT_m according to ($1a$):

$$RT_m = \frac{2a^2}{\beta} n\omega \left[-\frac{(1-z)^5(1-3z)(1-3y)}{4(y-z)^2(6z^2-8z+3-y)} + \frac{(1-z)^4(1-3z)^2(1-y)}{4(y-z)^2(6z^2-8z+3-y)} \right],$$

as $n\omega(\varphi + x) = z$ and $(1 + nx)\omega = y$. Reduction yields:

$$RT_m = \frac{2a^2}{\beta} n\omega \frac{(1-z)^4(1-3z)}{4(y-z)^2(6z^2-8z+3-y)} \left[1-3z)(1-y)-(1-z)(1-3y) \right].$$

The expression between [ ] is $= 2(y-z)$, hence, $\frac{n}{\beta}$ being $\frac{1}{b_1}$, we get:

$$RT_m = \frac{a^2\omega}{b_1} \frac{(1-z)^4(1-3z)}{(y-z)(6z^2-8z+3-y)}.$$

Let us express this in T_1, the critical temperature of one component. ($T_1 < T_2$). We find·

$$T_1 = \frac{8}{27} \frac{a_1}{b_1} = \frac{8}{27} \frac{a^2\varphi^2}{b_1},$$

as $\frac{\sqrt{a_1}}{a} = \varphi$ was put. At last we get:

$$\frac{T_m}{T_1} = \frac{27}{8} \frac{\omega}{\varphi^2} \frac{(1-z)^4(1-3z)}{(y-z)(6z^2-8z+3-y)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now

$$z = n\omega(\varphi + x) \quad ; \quad y = (1 + nx)\omega,$$

from which we solve.

$$n\omega = \frac{z}{\varphi + x} \quad ; \quad y = \omega + \frac{xz}{\varphi + x},$$

hence:

$$\omega = y - \frac{xz}{\varphi + x} \quad ; \quad \frac{1}{n} = \frac{y}{z}(\varphi + x) - x \quad . \quad . \quad . \quad . \quad (5)$$

Now ω and n have been expressed in y and z, as $(\varphi + x)_m$ and x_m had already been expressed in y and z by (2) and (3).

As further:

$$1 + n = 1 + \frac{\beta}{b_1} = \frac{b_2}{b_1} = \frac{\theta}{\pi},$$

and

$$1 + \frac{1}{\varphi} = 1 + \frac{a}{\sqrt{a_1}} = \frac{\sqrt{a_2}}{\sqrt{a_1}} = \frac{\theta}{\sqrt{\pi}},$$

when $\theta = T_2 : T_1 = \frac{a_2}{b_2} : \frac{a_1}{b_1}$ and $\pi = p_2 : p_1 = \frac{a_2}{b_2^2} : \frac{a_1}{b_1^2}$, we have also:

$$\theta = \frac{\left(1 + \frac{1}{\varphi}\right)^2}{1 + n} \quad ; \quad \pi = \frac{\left(1 + \frac{1}{\varphi}\right)^2}{(1 + n)^2}, \quad . \quad . \quad . \quad . \quad (6)$$

so that also θ and π can be expressed in y and z.

Reversely we may now also think the corresponding values of ω, x and T_m to be solved *for any given pair of values of* π and θ, though *explicitly* this is impossible, so that we shall have to be satisfied with the set of equations from (2) to (6).

The further discussion of these equations, particularly with regard to the branch C_0A of the plaitpoint line, in connection with the *longitudinal plait,* will be found in the paper, which will shortly appear in the Arch. Teyler. There the course of the *pressure* is also examined, which we no further discuss here. It is only desirable to calculate the data for the "third" critical temperature C_0, viz. x_0 and T_0 — not because these data are indispensable for the following considerations, but because KEESOM includes them in his considerations, and it is profitable in any case to know something concerning the relation $\frac{T_0}{T_1}$ or $\frac{T_0}{T_2}$.

As $v = b$ for the point C_0, so $y = \frac{b}{v} = 1$, and the equation of the v,x-projection of the plaitpoint line (Aug. 17, 1905, p. 146; Teyler I and II), viz.

$$(1-z)^3(1-2x-3x(1-x)n\omega)+3(\varphi+x)(1-y)^2(1-z)(1-2z)+ \\ +\frac{(\varphi+x)^3(1-y)^3(1-3y)}{x(1-x)}=0,$$

is reduced to

$$1-2x_0-3x_0(1-x_0)n\omega_0 = 0,$$

or as $y = (1+nx)\,\omega$, and hence $\omega_0 = \frac{1}{1+nx_0}$, to

$$(1-2x_0)(1+nx_0)-3x_0(1-x_0)n = 0,$$

from which follows

$$x_0 = \frac{(n+1)-\sqrt{n^2+n+1}}{n} \quad \ldots\ldots \quad (7)$$

From this is seen that the situation of C_0 depends only on the value of n or $1+n=\frac{b_2}{b_1}$.

The corresponding value of T_0 is found from $(1a)$. For $y=1$ we find:

$$RT_0 = \frac{2a^2\omega_0}{b_1}\,x_0\,(1-x_0)(1-z_0)^2,$$

in which $\omega_0 = \frac{1}{1+nx_0}$ and $z_0 = n\omega_0\,(\varphi + x_0)$.

As $T_1 = \frac{8}{27}\frac{a^2\varphi^2}{b_1}$ (see above), we have:

$$\frac{T_0}{T_1}=\frac{27}{4}\frac{\omega_0}{\varphi^2}x_0\,(1-x_0)\,(1-z_0)^2 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Hence we can immediately calculate x_0 and T_0 from (7) and (8) for any given set of values of θ and π, or φ and n.

3. For our case (a_1 small) it is now important to know, when a minimum occurs in the plaitpoint line $C_0\,C_2$, when not. For this purpose we shall derive the condition that the minimum is to appear exactly in the point C_2. Evidently this condition will then indicate the limit between the two cases that there occurs a minimum in the neighbourhood of C_2 or not — in other words whether the line of the plaitpoint temperatures in C_2 descends first and rises later on to T_0 in C_0; or whether there is an immediate rise from T_2 to T_0. (We call to mind that with us T_2 is always the *highest* of the two critical temperatures T_1 and T_2).

Now $y=\frac{b}{v}=\frac{1}{3}$ in the point C_2, while $x=1$. Hence equation (2) passes into

$$(\varphi+1)^2=\frac{(1-z)^4\,(1-3z)^2}{4\times{}^2/_3\,({}^1/_3-z)^2\,(6z^2-8z+2\,{}^2/_3)}=\frac{81}{16}\frac{(1-z)^4}{(2-3z)^2},$$

from which follows:

$$\varphi+1=\frac{9}{4}\frac{(1-z)^2}{2-3z},$$

hence

$$\frac{\sqrt{a_2}}{\sqrt{a_1}}=1+\frac{1}{\varphi}=9\,\frac{(1-z)^2}{(1-3z)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

From

$$z=n\omega\,(\varphi+x)$$

follows further, as $\omega=\frac{b_1}{v}=\frac{b_2}{v}\times\frac{b_1}{b_2}=\frac{1}{3}\frac{1}{1+n}$ and $x=1$:

$$z=\frac{1}{3}\frac{n}{1+n}\,(\varphi+1)=\frac{3}{4}\frac{n}{1+n}\frac{(1-z)^2}{2-3z}.$$

This yields:

$$\frac{1+n}{n}=\frac{3}{4}\frac{(1-z)^2}{z(2-3z)},$$

or

$$\frac{b_2}{b_1}=1+n=\frac{3\,(1-z)^2}{(1-3z)\,(3-5z)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

When we put:

$$\sqrt{\frac{a_2}{a_1}} = \varkappa \quad ; \quad \frac{b_2}{b_1} = \lambda,$$

the simple relation

$$\lambda \gtreqless \frac{\varkappa}{3+2\sqrt{\varkappa}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

follows from (a) and (b) after some reduction, in which the sign $>$ refers to the existence of a minimum in the neighbourhood of C_2.

The condition (c) found by us is quite identical with that, which we derived before from the formula for $\frac{1}{T_1}\left(\frac{dT_x}{dx}\right)_0$ found by us (Aug. 17, 1905, p. 150 and Jan. 25, 1906, p. 580). This condition was:

$$\theta < \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2}.$$

With this difference, however, that we then considered $\frac{1}{T_1}\left(\frac{dT_x}{dx}\right)_0$ at C_1, whereas we have now examined the branch of the plaitpoint line which starts from C_2, so that we have to calculate $\frac{1}{T_2}\left(\frac{dT_x}{dx}\right)_1$, and to derive the condition of the minimum from this. But it is immediately seen that it is obtained by substituting $\frac{1}{\theta}$ for θ and $\frac{1}{\pi}$ for π in the above condition.

So we find:

$$\frac{1}{\theta} < \frac{\frac{4}{\pi\sqrt{\pi}}}{\left(\frac{3}{\sqrt{\pi}}-1\right)^2},$$

or

$$\theta > \frac{\sqrt{\pi}(3-\sqrt{\pi})^2}{4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c')$$

And it appears immediately that (c) is identical with (c'), when we substitute $\frac{\theta^2}{\pi}$ for $\varkappa^2$ and $\frac{\theta}{\pi}$ for λ in (c).

This furnishes a good test, both of the accuracy of the above derived formula (c), and of the condition (c'), derived by us before.

Let us now examine what values of λ and $\varkappa$ correspond according to the condition (c), so that the minimum still appears exactly in C_2. The corresponding values of z required for the calculation of T_0, may be found from (a), giving:

$$z = \frac{1}{3}\,\frac{\sqrt{\varkappa}-3}{\sqrt{\varkappa}-1}.$$

The subjoined table combines the calculated values. We call attention to the fact that the minimum in the neighbourhood of C_2 can only belong to the branch C_2C_0 for type I ($\theta >$ the double point value), and never to the branch C_2C_1 for type II or III ($\theta <$ the double point value). For $T_2 > T_1$ being put, the minimum on C_2C_1 cannot possibly lie at C_2, but it can lie in the neighbourhood of C_1.

	$\varkappa=\sqrt{\frac{a_2}{a_1}}$	$\lambda=\frac{b_2}{b_1}$	$\theta=\frac{\varkappa^2}{\lambda}$	$\pi=\frac{\varkappa^2}{\lambda^2}$	x_1	$\frac{T_0}{T_1}$	$\frac{T_0}{T_2}=\frac{T_0}{T_1}\times\frac{1}{\theta}$
$s={}^1/_3$	∞	∞	∞	∞	0	∞	1 (Case $a_1=0$)
${}^1/_6$	25	$1\,{}^{12}/_{13}$	325	169	0,279	364	1,12
${}^1/_9$	16	$1\,{}^5/_{11}$	176	121	0,365	209	1,19
0	9	1	81	81	0,500	108	$1\,{}^1/_3$
$-{}^1/_3$	4	${}^4/_7$	28	49	0,694	—	—
-1	$2\,{}^1/_4$	${}^3/_8$	$13\,{}^1/_2$	36	0,800	$30\,{}^3/_8$	$2\,{}^1/_4$
$\mp\infty$	1	${}^1/_5$	5	25	0,896	—	—
${}^5/_3$	${}^1/_4$	${}^1/_{16}$	1	16	0,968	9,30	9,30

That is to say: for a gas *without cohesion* as one of the components of the mixture ($a_1=0, \varkappa=\infty$) λ would have to be larger than the limiting value ∞, for a minimum to appear in the line $C_2\,C_0$ in the neighbourhood of C_2. (Then ${}^{T_0}/_{T_2}<1$ would be at the same time). For finite values of λ this cannot be satisfied, and the line C_0C_2 proceeds with $T_0 > T_2$ without a minimum.

For a gas with *feeble cohesion,* where e.g. $\varkappa=\sqrt{\frac{a_2}{a_1}}=16$, $\lambda=\frac{b_2}{b_1}$ must be $> 1\,{}^5/_{11}$, for a minimum to appear. ${}^{T_0}/_{T_2}$ is then $< 1{,}19$.

For He — H_2 $\frac{a_2}{a_1}$ is about 175, hence $\varkappa=13{,}2$ according to an estimation of Keesom (These Proc., March 28, 1907, p. 661; Ibid. April 25, 1907, p. 794). To this corresponds according to formula (c) the limiting value $\lambda=1{,}29$. Now Keesom estimated (loc. cit.) this value at about 2 for He — H_2, and 2 being $> 1{,}29$, there is a minimum in the plaitpoint line in the case of He — H_2. This minimum can be fully calculated by the aid of the formulae (2) to (8). The value of ${}^{T_0}/_{T_2}$ is then smaller than about 1,25.

For $\varkappa = 2^1/_4$, λ must be $> {}^3/_8$, and then ${}^{T_0}/_{T_2} < 2^1/_4$. Etc., etc.

The larger therefore the value of a_1 — the smaller in other words the value of $\varkappa$ — the smaller also the limiting value of λ, above which a minimum is to be expected, the sooner this will therefore appear, and at comparatively large corresponding values of ${}^{T_0}/_{T_2}$.

But as we already observed in § 1, all this refers only to the existence or non-existence of a *minimum* in the line $C_0\, C_2$. *That* this line has the shape in question, depends on quite different circumstances — viz., as I already showed in June 21, 1905, p. 33—48 for $b_1 = b_2$, and further extended to the general case in later papers (particularly TEYLER I), it depends only on this, whether for the given value of π the value of θ is found above that at which the *plaitpoint line* has a *double point* or not. And the criterion for this is fig. 1 of Oct. 25, 1906 (see also TEYLER II). If we are *above* the limiting line $DBPAC'$, we are in the region of type I, where one of the branches of the plaitpoint line runs from C_0 to C_2 (the other from A to C_1 — see e.g. fig. 1 of Juni 21, 1905 and fig. 1 of Jan. 25, 1906). And *below* the limiting line we are in the region of type II (or III), where the branches of the plaitpoint line are $C_1\, C_2$ and AC_0. But for all this consult the papers cited.

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APPENDIX. After I had written the above considerations, the Continuation of the last cited paper by K. ONNES and KEESOM appeared in These Proceedings, April 25, 1907, p. 795—798. There a condition is derived for the appearance of a minimum plaitpoint temperature, which is identical with that which I published Jan. 25, 1906 (formula (3), p. 581), at which result also VERSCHAFFELT (These Proc., April 24, 1906, p. 751) arrived a month later.

For on p. 796 K. O. and KEESOM give the condition (see formula (2)):

$$\sqrt[4]{\frac{a_2}{a_1}} = \frac{1}{3}\left[-1 + \sqrt{1 + 3\, {}^{b_2}/_{b_1}}\right].$$

Now in my notation ${}^{a_2}/_{a_1} = {}^1/_{\varkappa^2}$ (see above; I denote viz. the component with the smallest value of a by the index 1; KEESOM does the reverse). Further ${}^{b_2}/_{b_1} = {}^1/_\lambda$, so that the above formula passes into

$$\sqrt{\frac{1}{\varkappa}} = \frac{1}{3}\left[-1 + \sqrt{1 + {}^3/_\lambda}\right],$$

from which follows:

$$\lambda = \frac{x}{3+2\sqrt{x}},$$

being my above formula (c). And concerning this we have just proved that it is identical with my relation and that of VERSCHAFFELT (Jan. and April 1906), viz.

$$\theta = \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2},$$

which is of general application, irrespective whether the branch of the plaitpoint line starts from C_2 towards C_1 or towards C_0. As we already observed, this expression holds on the side of the component I, when $\theta = T_2/T_1$ and $\pi = p_2/p_1$, so for the branch starting from what is point C_1 with me. For C_2 (KEESOM's K_1) θ and π must simply be replaced by $1/\theta$ and $1/\pi$ (see above in § 3).

So in my opinion the footnote on p. 795 in the paper by K. O. and K. of April 25, 1907 is not accurate, for according to the above the conclusion of VERSCHAFFELT (and mine) does not require any qualification, because the formula [1]) given by us holds for any course of the plaitpoint line, irrespective of the fact whether the considered branch runs from C_2 to C_1 or to C_0. For the transition of the two types takes place gradually through the double point of the plaitpoint line, and hence the two types are analytically included in the same formula, so that only one expression exists for $\frac{dT_x}{dx}$, which holds equally for the two cases. And if any doubt should remain, this must be removed, when from the above the identity is seen between the relation derived last by K. O. and K., and the general one of VERSCHAFFELT and me.

It will be superfluous to observe that the so-called (homogeneous) "double *plaitpoint*" in the branch of the plaitpoint line C_0C_2, of which K. O. and K. speak, is identical with the fully discussed minimum and with the double point in the spinodal line, and should not be confounded with the "double *point*", found by me in the (whole) plaitpoint line, where the two branches of this line intersect, and which separates the two types I and II (or III), the data for which double point can be calculated for the general case only with great difficulty. (see Teyler I).

[1]) In the footnote on p. 795 it says maximum temperature; this must of course be minimum temperature.