Citation:

J.J. van Laar, On the shape of the plaitpoint curves for mixtures of normal substances, in:
KNAW, Proceedings, 8 I, 1905, Amsterdam, 1905, pp. 33-48

The points of contact of the three-pointed tangents of (F^n) *form a surface of order* $2(n-4)(n^3+2n^2+10n-12)$.

7. Through the tangent s in S to σ we can make to pass four tangent planes to the cubic cone of the principal tangents (§ 1). So S is a parabolic point on four surfaces of the pencil. Therefore σ is a fourfold curve on the locus of the parabolic points.

As the parabolic points of an F^n lie on a curve of order $4n(n-2)$ the locus under consideration is cut by each of the surfaces F^n in a curve of order $4n(n-2)+4n^2=8n(n-1)$.

The locus of the parabolic points of the surfaces of a pencil (F^n) *is a surface of order* $8(n-1)$.

Chemistry. — *"On the shape of the plaitpoint curve for mixtures of normal substances."* (Second communication). By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In a previous paper[1]), starting from VAN DER WAALS' equation of state, in which b is assumed to be independent of v and T, I have found for the equation of the *spinodal curves* at successive temperatures (l. c. p. 690):

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

and for that of the plaitpoint curve in its v, x projection (l.c. p. 695):

$$\underline{x(1-x)\theta^3\left[(1-2x)v-3x(1-x)\beta\right]+\sqrt{a}(v-b)^2\left[3x(1-x)\theta(\theta-\beta\sqrt{a})+\right.}$$

$$\underline{\left.+a(v-b)(v-3b)\right]}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this $\theta=\pi+\alpha(v-b)$, $\pi=b_1\sqrt{a_2}-b_2\sqrt{a_1}$, $\alpha=\sqrt{a_2}-\sqrt{a_1}$, and $\beta=b_2-b_1$.

The equations (1) and (2) hold for the so-called *symmetrical* case, where not only $b_{12}={}^1/_2(b_1+b_2)$ is assumed, but also $a_{12}=\sqrt{a_1a_2}$. These hypotheses lead to:

$$b=(1-x)b_1+xb_2 \quad ; \quad a=[(1-x)\sqrt{a_1}+x\sqrt{a_2}]^2.$$

The equation (1) had been given already before by VAN DER WAALS in implicit form[2]), for after some reduction his general equation

1) These Proc. April 22, 1905, p. 646—657.

2) Cont. II, p. 45; Arch. Néerl. 24, p. 52 (1891).

passes really into (1) after substitution of the values of $\frac{da}{dx}$, $\frac{db}{dx}$, $\frac{d^2a}{dx^2}$ and $\frac{d^2b}{dx^2}$ in accordance with the above hypotheses.

But the equation (2) may be said to have been derived here for the first time in the above simple form. It is true that VAN DER WAALS gave a differential equation of this curve [1]), and derived an *approximate* rule for its shape [2]), but he did not arrive at a general final expression. Nor has KORTEWEG arrived at it in his very important papers: "Sur les points de plissement" and "La théorie générale des plis, etc." [3]) In his final equation (73) (l.c. p. 361) there occur, besides T, still several functions $\varphi(v)$, $\zeta(v)$, $\psi(v)$ and $\chi(v)$, which have been given respectively by the equations (37), (38), (40) and (74) (l. c. p. 350 and 361). KORTEWEG's equation is one of the 9^{th} degree with respect to v, but it is easy to see that it may be reduced to one of the 8^{th} degree (l. c. p. 361). It appears from our derivation that this degree may be reduced to the 4^{th}. In a later paper [4]) KORTEWEG confines himself to a full discussion of the plaitpoints in the neighbourhood of the borders of the ψ-surface.

I think that one of the reasons for failure in this direction is due to the intricate form of the differential equation of the plaitpoint curve, when we use the ψ-function. The ζ-function on the other hand leads to simpler expressions. Already the differential equation for the spinodal line at given temperature, viz. $\left(\frac{\partial^2\zeta}{\partial x^2}\right)_{p,T}=0$ or $\left(\frac{\partial\mu_1}{\partial x}\right)_{p,T}=0$, is much simpler than the corresponding expression in ψ. And to get the plaitpoint curve, we have only to combine $\left(\frac{\partial\mu_1}{\partial x}\right)_{p,T}=0$ with $\left(\frac{\partial^2\mu_1}{\partial x^2}\right)_{p,T}=0$.

2. We shall now examine the shape of the curves given by (1) and (2) more closely, and specially for the case that $\beta=0$, i. e. $b_1=b_2=b$. The calculations are rendered very simple in this way, and it is obvious from the adjoined figs. 1—4, that when b_1 is not $=b_2$, so β not $=0$, the results will be modified only quantitatively, but by no means qualitatively. We shall come back to this in a following paper.

1) Verslagen Kon. Akad. Amsterdam, 4, p. 20—30 en 82—93 (1896).
2) Id. 6, p. 279—303 (1898).
3) Arch. Néerl. 24, p. 57—98 en 295—368 (1891).
4) These Proc. Jan. 31, 1903, p. 445.

As $\theta = \pi + a(v - b) = a v - \beta \sqrt{a}$ passes into av for $\beta = 0$, we may write for (1):

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

and (2) is reduced to:

$$x(1-x)a^2v^3\left[(1-2x)v\right] + \sqrt{a}(v-b)^2\left[3x(1-x)a^2v^2 + a(v-b)(v-3b)\right] = 0. \quad (2a)$$

Let us put these equations into a more homogeneous form.

As $a = [\sqrt{a_1} + x(\sqrt{a_2} - \sqrt{a_1})]^2 = (\sqrt{a_1} + x\alpha)^2$, we may write for $(1a)$:

$$RT = \frac{2}{v}\left[x(1-x)\,\alpha^2 + (\sqrt{a_1} + x\,\alpha)^2 \left(1 - \frac{b}{v}\right)^2 \right]$$

$$= \frac{2\alpha^2}{v}\left[x(1-x) + \left(\frac{\sqrt{a_1}}{\alpha} + x\right)^2 \left(1 - \frac{b}{v}\right)^2 \right].$$

If we now put:

$$\frac{\sqrt{a_1}}{\alpha} = \varphi \quad ; \quad \frac{b}{v} = \omega,$$

this last equation becomes:

$$RT = \frac{2\alpha^2}{b}\,\omega \left[x(1-x) + (\varphi + x)^2 (1-\omega)^2 \right].$$

Let us now introduce the "third" critical temperature T_0. This temperature is the plaitpoint temperature at $v = b$, i. e. that at which the limiting curve lying in the limiting plane $v = b$ (see fig. 1 of my previous paper cited above) reaches its maximum, and is represented by $(\omega = 1)$:

$$RT_0 = x_c(1 - x_c)\,\frac{2\alpha^2}{b}.$$

But as in the case $b_1 = b_2$ for x_c the value $1/2$ is found (the maximum of the now parabolic curve), we get:

$$RT_0 = \frac{1/2\,\alpha^2}{b}.$$

Our equation for RT becomes therefore:

$$RT = 4\,RT_0\,\omega \left[x(1-x) + (\varphi + x)^2 (1-\omega)^2 \right].$$

And if henceforth all temperatures are expressed in multiples of T_0, we have finally, putting

$$\frac{T}{T_0} = \tau,$$

$$\tau = 4\,\omega \left[x(1-x) + (\varphi + x)^2 (1-\omega)^2 \right] \quad . \quad . \quad (1b)$$

3*

In this simple form the equation is very suitable for calculating successive spinodal curves. It is of the *second* degree with respect to x, of the *third* degree with respect to ω. For a given value of τ we have therefore only to put successively $\omega = 1$, 0,9, 0,8 etc. down to 0, and then we find the corresponding values of x by solution of ordinary quadratic equations.

The equation (2a) becomes after division by $x(1-x)\,\alpha^3 v^4$:

$$(1-2x) + \frac{\sqrt{a}}{\alpha}\left(1-\frac{b}{v}\right)^2\left[3 + \frac{{}^a/_{\alpha^2}\,(1-{}^b/_v)\,(1-{}^{3b}/_v)}{x\,(1-x)}\right] = 0,$$

i. e. as $\dfrac{\sqrt{a}}{\alpha} = \dfrac{\sqrt{a_1}}{\alpha} + x = \varphi + x$

$$(1-2x) + (\varphi + x)(1-\omega)^2\left[3 + \frac{(\varphi+x)^2}{x\,(1-x)}(1-\omega)(1-3\omega)\right] = 0\,.\,.\,(2b)$$

This equation of the plaitpoint curve is of the *third* degree with respect to x, of the *fourth* degree with respect to ω.

3. Before discussing the equations (1b) and (2b) more fully, we shall first derive a few relations between T_0, T_1 and T_2.

As $RT_0 = \dfrac{{}^1/_2\,\alpha^2}{b}$ (see above) and $RT_1 = \dfrac{8}{27}\dfrac{a_1}{b}$, we find immediately:

$$\frac{T_1}{T_0} = \frac{16}{27}\frac{a_1}{\alpha^2} = \frac{16}{27}\varphi^2.$$

From this follows that for values of $\varphi < {}^3/_4\sqrt{3}\ (= 1{,}30)$ T_1 will be $< T_0$; i. e. the lower critical temperature of the two components will then be lower than the critical temperature of mixing of the two liquid phases at $v = b$.

As $\varphi = \dfrac{\sqrt{a_1}}{\sqrt{a_2}-\sqrt{a_1}}$, so $\dfrac{1}{\varphi} = \dfrac{\sqrt{a_2}}{\sqrt{a_1}} - 1$, and we have evidently:

$$\frac{T_2}{T_1} = \left(1 + \frac{1}{\varphi}\right)^2.$$

For $\varphi = 0$ is $T_2 = \infty \times T_1$; for $\varphi = \infty$ is $T_2 = T_1$. For $\varphi = {}^3/_4\sqrt{3}$ (see above) ${}^{T_2}/_{T_1} = (1 + {}^4/_9\sqrt{3})^2 = {}^1/_{27}\,(43 + 24\sqrt{3}) = 3{,}13$.

It will also prove important to know the amount of the *pressure* for all points of the spinodal curves. For this purpose we reduce the equation:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

to

$$p = \frac{RT}{v(1-{}^{b}/_{v})} - \frac{(\sqrt{a_1}+xa)^2}{v^2} = \frac{RT}{v(1-\omega)} - \frac{a^2}{v^2}(\varphi + x)^2.$$

This becomes on account of $a^2 = 2bRT_0$ (see above) and ${}^{T}/_{T_0} = \tau$:

$$p = \frac{RT_0}{b}\omega\left\{\frac{\tau}{1-\omega} - 2\omega(\varphi + x)^2\right\}.$$

Let us express p in the critical pressure p_1. (As, namely, the pressure p_0 corresponding to T_0 $(v = b)$ is evidently $= \infty$, p cannot be expressed in p_0). As $p_1 = {}^{1}/_{8}\frac{RT_1}{b}$ and $\frac{T_1}{T_0} = \frac{16}{27}\varphi^2$, $p_1 = \frac{2}{27}\frac{RT_0}{b}\varphi^2$, hence — when we put

$$\frac{p}{p_1} = \pi:$$

$$\pi = \frac{27}{2}\frac{\omega}{\varphi^2}\left[\frac{\tau}{1-\omega} - 2\omega(\varphi + x)^2\right] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation may be used, when τ is already known from $(1b)$. If this value is, however, substituted, we get:

$$\pi = \frac{27}{\varphi^2}\frac{\omega^2}{1-\omega}\left[2x(1-x) + 2(\varphi+x)^2(1-\omega)^2 - (\varphi+x)^2(1-\omega)\right],$$

i. e.

$$\pi = \frac{27}{\varphi^2}\frac{\omega^2}{1-\omega}\left[2x(1-x) + (\varphi+x)^2(1-\omega)(1-2\omega)\right] \quad . \quad . \quad . \quad . \quad (3a)$$

4. Better than descriptions and calculations the adjoined figures 1—4 represent the different relations which may present themselves in the discussion of $(1b)$ and $(2b)$, combined with 3 or $(3a)$. We shall therefore confine ourselves in the following to what is strictly indispensable.

Two principal types occur, according as $\varphi < 1{,}43$ or $> 1{,}43$. Fig. 1 with $\varphi = 1$ is a representative of the one type, fig. 2 with $\varphi = 2$ of the other. The transition case $\varphi = 1{,}43$ is represented in fig. 4.

a. *Description of the case* $\varphi = 1$ (fig. 1 and $1a$).

There are *two* plaitpoint curves, one of which extending from C_0 to C_2, the other from C_1 to A. The latter, however, may only be realized down to a point between C_1 and R_1, where it is touched by the spinodal line $\tau = 0{,}63$ [1]).

[1]) See KORTEWEG, l. c. p. 305 (fig 12) and plate F_1 to F_5. (The plaitpoint has already disappeared in the limiting line $v = b$ in our case). R_1 is a so-called point de plissement double hétérogène. Cf. also VAN DER WAALS, These Proc. V, 310, Oct. 25, 1902.

Beyond the point R_1 the temperature, and with it also the pressure, decreases, as is to be seen from the succession of the different spinodal curves, so that in the p,T-diagram (fig. 1a) the plaitpoint curve C_1R_1A shows a cusp at R_1, and begins to run back.

It is known that this case is realized with mixtures of C_2H_6 and CH_3OH, ether and water (KUENEN), etc. It is the *principal type I*, as I have fully described it in one of my two preceding papers [1]).

Remarkable and quite unexpected is the fact that this type may be realized for mixtures of *normal* substances. It was formerly believed that such deviating plaitpoint curves were only possible when at least one of the two substances is anomalous. This, however, seems not to be the case; more and more the conviction gains ground with me that the anomaly of one or of both components only *accentuates* the phenomena *sharper* or brings them into *attainable* regions of temperature.

It is also striking in fig. 1a, that the curve $C_0\ C_2$ has the same appearance, viz. with an inflection in the middle part, as the typical curve as observed by KUENEN for $C_2H_6 + CH_3OH$ (see fig. 1 of my just cited paper). Only in our case there is not yet a pronounced maximum and minimum, as with the mixtures of C_2H_6 with the strongly *anomalous* substance CH_3OH.

The type of fig. 1 occurs for comparatively small values of φ. According to the equation given in § 3 the proportion $T_2/T_1 = 4$ corresponds with $\varphi = 1$. The critical temperatures of the two components must, therefore, lie comparatively far apart.

As $T_1/T_0 = \frac{16}{27}$, T_0 is considerably higher than T_1. If we put $T_0 = 1$, as has been done in the figure, then $T_1 = 0{,}59$ and $T_2 = 2{,}37$.

b. *Some mathematical and numerical details.*

The plaitpoint curve C_0C_2 touches the line $x = {}^1/_2$ in C_0, the curve AC_1 touches the line $x = 0$ in A. Moreover the curve C_0C_2 touches the line $x = {}^1/_2$ once more in D, and it does so at $\omega = {}^2/_3$ ($v = 1{,}5\ b$). In C_1 and C_2 no contact takes place.

When φ becomes < 1, and approaches to 0 (T_2/T_1 then becomes larger and larger and approaches to ∞), then the curve C_1A approaches the straight line $x = 0$ more and more and the curve C_0C_2 the dotted curve in the figure, which continues to present a clearly

1) These Proc. VII p. 636—638, April 22, 1905

pronounced inflection point up to the last [1]). For values of $\varphi > 1$, the curve C_0C_2 lies partially on the left of the curve $x = 1/_2$, and the point of contact at D passes into two points of intersection.

By an approximate solution of $(2b)$ and substitution in (1^b) and (3) of the values found, the following points of the two plaitpoint curves are calculated. (The other values of ω or x are either imaginary or do not satisfy).

$\underline{\varphi = 1}$

Curve C_0C_2

$x = 0{,}5$	0,6	0,7	0,8	0,9	1
$\omega = 1$	0,49	0,43	0,39	0,36	0,33
$\tau = 1$	1,78	1,98	2,13	2,26	2,37
$\pi = \infty$	6,74	5,75	5,05	4,51	4

Curve C_1A

$\omega = 0{,}33$	0,4	0,5 [2])	0,6	0,7	0,8	0,9	1
$x = 0$	0,021	0,041	0,042	0,023	0,010	0,0017	0
$\tau = 0{,}59$	0,63	0,62	0,51	0,33	0,16	0,042	0
$\pi = 1$	1,15	1,08	0	—3,09	—3,64	—16,9	- 27

It is seen that the pressure begins to be *negative* for points in the neighbourhood of A. This is not remarkable; also for a simple substance the points of inflection in the ideal isotherms reach to within the region of the negative pressures. Though the pressures in some points on the *spinodal* curve are negative, this is no reason why those on the connodal curves should be so.

The limits of the region of negative pressures on the spinodal curves may be easily fixed (see the dotted curves in fig. 1) by solution of the equation (see $(3a)$)

$$2x(1-x) = (\varphi + x)^2 (1-\omega)(2\omega - 1).$$

If we put here $(1-\omega)(2\omega-1) = \theta$, we find:

$$x = \frac{(1-\varphi\theta) \pm \sqrt{1 - 2\varphi(\varphi+1)\theta}}{2+\theta}.$$

In this way we calculate for $\varphi = 1$:

$$\begin{array}{lllllll} \omega = & 1 & 0{,}9 & 0{,}8 & 0{,}7 & 0{,}6 & 0{,}5 \\ x = & \begin{cases} 0 \\ 1 \end{cases} & \begin{matrix} 0{,}04^5 \\ 0{,}84 \end{matrix} & \begin{matrix} 0{,}07 \\ 0{,}75^5 \end{matrix} & \begin{matrix} 0{,}07 \\ 0{,}75^5 \end{matrix} & \begin{matrix} 0{,}04^5 \\ 0{,}84 \end{matrix} & \begin{matrix} 0 \\ 1. \end{matrix} \end{array}$$

That π approaches to -27 for $x = 0$, $\omega = 1$, $\tau = 0$ follows immediately from (3). For as $\frac{\tau}{1-\omega}$ approaches to 0, as we shall prove presently, $\pi = \frac{27}{2}\frac{1}{\varphi^2}\left(-2\varphi^2\right) = -27$, independent of the value of φ.

[1]) For this plaitpoint curve $\varphi = 0$ the following points are easily calculated:

$$\begin{array}{lllllll} \omega = & 0{,}9 & 0{,}8 & 0{,}7 & 0{,}6 & 0{,}5 & 0{,}4 \\ x = & 0{,}507 & 0{,}528 & 0{,}567 & 0{,}623 & 0{,}712 & 0{,}853 \end{array}$$

The equation $(2b)$, viz., passes then into the following quadratic equation in $x\omega$:

$$x^2\omega^2(9 - 10\omega + 3\omega^2) - 3x\omega(2-\omega) + 1 = 0.$$

The other value for x is always > 1.

[2]) The maximum lies at $\omega = 0{,}54$; x is then about $= 0{,}043$.

In this we must notice that in the immediate neighbourhood of the point A, π increases with the utmost rapidity from -27 to $+\infty$, when we pass the above considered border curve; *in* the point A itself this transition takes of course place suddenly. For when $\omega = 1$, π approaches to $\frac{27}{\varphi^2}\frac{2x(1-x)}{1-\omega} = \infty$, according to (3*a*), *except* in the case that x is exactly $= 0$, when (see further) $\frac{2x(1-x)}{1-\omega} = 0$, the following term yielding then the finite value -27. This follows also from the figure, because the border curve, which separates positive from negative pressures, passes *through* the point A.

That on the plaitpoint curve the expressions $\frac{x}{1-\omega}$ and $\frac{\tau}{1-\omega}$ approach to 0 for $x = 0$, $\omega = 1$, $\tau = 0$ at A, follows from (2*b*). For putting $x = \Delta$ and $1 - \omega = \delta$, we get:

$$1 + \varphi\delta^2\left(3 - 2\frac{\varphi^2}{\Delta}\delta\right) = 0,$$

or as $3\varphi\delta^2$ may be neutralized by 1, $1 - 2\varphi^3\frac{\delta^3}{\Delta} = 0$, from which follows, that at the point A $\underline{\frac{\Delta}{\delta^3} = 2\varphi^3}$, so remains finite. So Δ is of the order δ^3, so that $\frac{a}{1-\omega} = \frac{\Delta}{\delta}$ really approaches to 0 at A. From this follows also the *contact*. And as according to (1*b*) τ approaches to $4(\Delta + \varphi^2\delta^2) = \underline{4\varphi^2\delta^2}$ (Δ being of the order δ^3) for $x = 0, \omega = 1$, $\frac{\tau}{1-\omega}$ approaches to 0 at A.

In the same way the plaitpoint curve C_0C_2 touches the line $x = {}^1/_2$ for $x = {}^1/_2, \omega = 1$. For, for $x = {}^1/_2(1 + \Delta), \omega = 1 - \delta$ equation (2*b*) becomes:

$$-\Delta + (\varphi + {}^1/_2)\,\delta^2\left[3 - 8(\varphi + {}^1/_2)^2\delta\right] = 0,$$

which appoaches to $-\Delta + 3(\varphi + {}^1/_2)\,\delta^2 = 0$, yielding $\underline{\frac{\Delta}{\delta^2} = 3(\varphi + {}^1/_2)}$, so again finite. So Δ is now of the order δ^2, and so $\frac{\Delta}{\delta}$ again $= 0$, which proves the contact at C_0.

I call attention to the fact, that on account of the small values of Δ a large portion of the curve C_0C_2 from C_0 as far as beyond the point D may be calculated very accurately, by writing for (2*b*) ($\varphi = 1$):

$$-\Delta + {}^3/_2 (1-\omega)^2 \left[3 - 9 (1-\omega)(3\omega - 1) \right],$$

so that $$\Delta = {}^3/_2 (1-\omega)^2 \left[1 - 3 (1-\omega)(3\omega - 1) \right],$$

From this follows e.g. for $\omega = 0{,}9$, $0{,}8$, $0{,}7$, $0{,}6$ resp., for Δ 0,022, 0,029, 0,004, 0,029.

The contact at D. If we put in (2*b*) $x = {}^1/_2$, then $1 - 2x = 0$, and hence:

$$(\varphi + {}^1/_2)(1-\omega)^2 \left[3 + 4 (\varphi + {}^1/_2)^2 (1-\omega)(1-3\omega) \right] = 0\,.$$

This yields besides $\omega = 1$ (the point C_0), also:

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

hence:

$$\omega = {}^2/_3 \pm {}^1/_3 \sqrt{1 - \frac{9}{(2\varphi+1)^2}}\,.$$

For $\varphi = 1$ this yields two equal roots $\omega = {}^2/_3$, which proves the contact at D. For $\varphi < 1$ the roots become imaginary, so that then $C_0 C_2$ no longer cuts the line $x = {}^1/_2$, but keeps continually on its right, whereas for $\varphi > 1$ two points of intersection are always found. So is e.g. for $\varphi = 2$ $\omega = {}^{14}/_{15}$ (close to C_0) and $\omega = {}^2/_5$ (lying on the other branch between C_1 and C_2 (see fig. 2)).

In order to facilitate the tracing of the different *spinodal* lines, it is to be recommended to fix the limiting values of τ for $x = 0$, $x = 1$, $\omega = 1$, $\omega = {}^1/_3$. Also for $x = {}^1/_2$ it is easy to calculate τ. From (1*b*) follows e.g. for $x = 0$, $\varphi = 1$:

$$\tau = 4\omega (1-\omega)^2.$$

This yields:

$\omega =$	1	0,9	0,8	0,7	0,6	0,5	0,4	0,333	0,3	0,2	0,1
$\tau =$	0	0,036	0,128	0,252	0,384	0,50	0,576	0,593	0,588	0,512	0,324

For $x = 1$ these values become simply 4 times larger, $(\varphi + x)^2$ then being $= 4$.

For $x = {}^1/_2$ we get,

$$\tau = \omega \{1 + 9 (1-\omega)^2\},$$

yielding:

$\omega =$	1	0,95	0,9	0,8	0,7	0,6	0,5	0,4	0,33	0,3
$\tau =$	1	0,971	0,981	1,09	1,27	1,46	$1{,}62^5$	1,70	1,67	1,62.

For $\omega = 1$ we get simply:

$$\tau = 4x (1-x),$$

from which follows:

$x=0$	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau=0$	0,36	0,64	0,84	0,96	1	0,96	0,84	0,64	0,36	0.

Finally we get for $\omega = {}^1/_3$:

$$\tau = {}^4/_3 \left[x(1-x) + {}^4/_9 (x+1)^2 \right],$$

yielding:

$x=$ 0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau=$ 0,593	0,837	1,07	1,28	1,48	1,67	1,84	1,99	2,13	2,26	2,37.

It appears from the diagram (see also above for $x = {}^1/_2$), that the temperature from C_0 to C_2 is not continually ascending, but that it shows a *minimum* very near C_0. This causes the spinodal line $\tau = 1$ *not* to pass through C_0, but to remain under it. The point C_0, where τ is also $=1$, is an isolated point belonging to that line. Just beyond C_0 the two branches of one and the same spinodal line intersect in a double point; beyond that place the course is normal; between C_0 and this intersection the spinodal line has two separate branches, one of which encloses the point C_0. Now the question arises, whether this will be the case for every value of φ. If we solve x from (1*b*), we get:

$$x^2(2\omega - \omega^2) - x\left(1 + 2\varphi(1-\omega)^2\right) + \left(\frac{\tau}{4\omega} - \varphi^2(1-\omega)^2\right) = 0 .$$

This gives for x two roots of the same value for given values of τ and ω, when

$$4\varphi(\varphi+1)(1-\omega)^2 + 1 - \tau(2-\omega) = 0.$$

The value of x is then:

$$x = \frac{{}^1/_2 + \varphi(1-\omega)^2}{\omega(2-\omega)}.$$

Now it follows from the value of the above given discriminant, that it becomes $=0$ for *two* values of ω. So two branches of a spinodal line intersect, when those values of ω become the same. From

$$4\varphi(\varphi+1)\omega^2 - \omega\left(8\varphi(\varphi+1) - \tau\right) + \left(4\varphi(\varphi+1) + 1 - 2\tau\right) = 0$$

follows, that ω has two roots of the same value, when

$$\frac{\tau^2}{1-\tau} = 16\varphi(\varphi+1) \quad ; \quad \omega = 1 - {}^1/_8 \frac{\tau}{\varphi(\varphi+1)}.$$

And τ being 1 at C_0, the minimum disappears only, when τ becomes $=1$ in the above expression. And this is evidently only the case for $\varphi = \infty$, i. e. when T_1 and T'_2 should have the same value. Hence in general there will always be found a minimum in the neighbourhood of C_0. For $\varphi = 1$ we find $\tau = 0,970$, $\omega = 0,94$, $x = 0,506$; for $\varphi = 2$ we find $\tau = 0,990$, $\omega = 0,98$, $x = 0,501$; etc. etc.

It may be easily demonstrated that in the neighbourhood of C_1 such a minimum never appears in our case. For from (1*b*) follows with $\tau = \frac{T_1}{T_0} = \frac{16}{27}\varphi^2$:

$$\frac{16}{27}\varphi^2 = 4\omega\left[x(1-x)+(\varphi+x)^2(1-\omega)^2\right].$$

After substitution of $x = \Delta$, $\omega = {}^1/_3(1+\delta)$, we get, neglecting Δ^2, which is justified by the result:

$$(1+\delta)\left[\frac{9}{4}\frac{\Delta}{\varphi^2}+\left(1+\frac{2\Delta}{\varphi}\right)(1-{}^1/_2\delta)^2\right]=1,$$

or as $\frac{1}{1+\delta}=1-\delta+\delta^2-\ldots$, and so $\frac{1}{1+\delta}-(1-{}^1/_2\delta)^2={}^3/_4\delta^2$:

$$\frac{9}{4}\frac{\Delta}{\varphi^2}+\frac{2\Delta}{\varphi}(1-{}^1/_2\delta)^2={}^3/_4\delta^2,$$

yielding:

$$\Delta={}^3/_4\delta^2:\left(\frac{9}{4\varphi^2}+\frac{2}{\varphi}\right)=3\delta^2:\left(\frac{9}{\varphi^2}+\frac{8}{\varphi}\right).$$

The spinodal line $T=T_1$ touches, therefore, the axis $x=0$ for every value of φ, and, at least on the assumptions made by us concerning a and b, a minimum can therefore never appear in the neighbourhood of C_1, in consequence of which the spinodal lines in the immediate neighbourhood of C_1 would enclose this point.

Finally some corresponding values of x and ω are subjoined, which determine the shape of the spinodal line $\tau=1$ ($T=T_0$). By solution of the quadratic equation

$$4\omega\left[x(1-x)+(1+x)^2\,1-\omega)^2\right]=1$$

follows immediately:

$\omega =$	1	0,8	0,7	0,6	0,5	0,4	0,33	0,3	0,2	0,1
$x =$	0,5	0,403	0,292	0,227	0,184	0,164	0,182	0,182	0,306	0,679
		0,743	1,004							

So this line cuts the axis $x=1$ for $\omega=0,7$, and henceforth only one solution satisfies. x becomes evidently 1 for $\omega(1-\omega)^2={}^1/_{16}$, yielding about $\omega=0,07$.

From the above derived equation $4\varphi(\varphi+1)(1-\omega)^2+1-\tau(2-\omega)=0$, which was the condition for two equal values of x, we find $\varphi=1,\tau=1$:

$$8\omega^2-15\omega+7=0,$$

from which, besides $\omega=1$, $\omega={}^7/_8$ follows. To this belongs then $x={}^{11}/_{21}=0,524$. Between $\omega=1$ and $\omega=0,875$ we find only imaginary values for x in the above table.

As to the spinodal line $T = T_1$ ($\tau = 0.59$), we calculate $x = 0{,}0019$ for $\omega = 0{,}30$, whereas $x = 0{,}006$ corresponds to $\omega = 0{,}40$.

As to the shape of the spinodal lines for great values of v (vapour branch) i. e. when τ and ω approach to 0, follows immediately from ($1b$):

$$\tau = 4\omega \left[x(1-x) + (\varphi + x)^2 \right] = 4\omega \left[\varphi^2 + (2\varphi + 1)x \right].$$

If we substitute $T/T_0 = T : \frac{{}^1/_2 a^2}{Rb}$ for τ, and $\frac{b}{v}$ for ω, we get:

$$RT = \frac{2a^2}{v} \left[\varphi^2 + (2\varphi + 1)x \right].$$

After substitution of $\varphi = \frac{\sqrt{a_1}}{a}$, this becomes:

$$v = \frac{2}{RT} \left[a_1 + (a_2 - a_1)x \right].$$

From this follows that the vapour branches of the spinodal lines in their v, x-projection will approach more and more to straight lines, which will cut the axes $x = 0$ and $x = 1$ at distances proportional to the quantities a_1 and a_2.

5. Let us now consider the second type, which occurs for $\varphi = 2$.

a. *Description of the case* $\varphi = 2$ (fig. 2 and fig. 2a).

The two plaitpoint curves of fig. 1, viz. C_0C_2 and C_1A have met for φ about 1,43 (see fig. 4), after which two new ones have been formed, now C_1C_2 and C_0A. This case, which is found for comparatively large values of φ, for which the proportion $\frac{T_2}{T_1}$ approaches more and more to unity, is the usual one or the normal one. It is the *principal type III*, as described in one of my two preceding papers [1]).

The region of negative pressures on the spinodal lines extends now all over the v, x-diagram, from $x = 0$ to $x = 1$, and is bounded by the two dotted curves (see fig. 2) above and below.

The spinodal line belonging to $\tau = 1{,}35$ touches now the curve C_0A in the point R_2. Again the plaitpoints are not realisable from a point between R_2 and C_0 to A (see the footnote in § 4 at **a.**)

Beyond R_2 the temperature and with it the pressure decreases, so that in the p, T diagram (see fig. 2a) the curve C_0R_2A *runs back*

[1]) l. c. p. 642—644.

again from R_2. In R_2 the pressure is already negative, and it becomes again $= -27\, p_1$ in A. (See § 4 at **b**).

When $\varphi = 2$, we find easily from the equations derived in § 3, that then $T_2/T_1 = 2^1/_4$ and $T_1/T_0 = {}^{64}/_{27}$. So if T_0 is again $=1$, then $T_1 = 2{,}37$ and $T_2 = 5{,}33$. Now T_1 is higher than T_0.

b. *Some mathematical and numerical details.*

Much having already been derived in § 4, it will suffice to give some few values.

Of the two plaitpoint curves the following points were calculated

$\varphi = 2$

$x =$ 0	0,15	0,2	0,3	0,4	0,5	0,6	0 7	0,8	0,9	1	Curve C_1C_2
$\omega =$ 0 33^3	0 39^5	0 40^3	0,41$^+$	0,41$^-$	0 40	0 39$^+$	0 37^4	0,35^9	0,34^7	0,33^8	
$\tau =$ 2 37	2 87	3,04	3,38	3 70	4,00	4 28	4 60	4,87	5,10	5,33	
$\pi =$ 1	1,46	1 62	1,90	2 11	2,25	2,32	2,37	2,36	2,33	2,25	

$x =$	0	0,01	0,1	0,2	0,3	0,4	0,5	Curve C_0A.
$\omega =$	1	0,91	0,81	0,78	0,80	0,85	0,933 and 1	
$\tau =$	0	0,15^5	0,81	1,23	1,35	1,26	1,04 and 1	
$\pi =$	—27	—17 3	—7,90	—5,16	—4,62	—3,98	49 and ∞	

The separation between the negative and positive pressures on the spinodal curves is given by

$$\begin{array}{llllll} \omega = 1 & 0{,}9 & 0{,}894 & 0{,}606 & 0{,}6 & 0{,}5 \\ x = \left\{\begin{array}{l} 0 \\ 1 \end{array}\right. \begin{array}{l} \\ \end{array} & \begin{array}{l} 0{,}31 \\ 0{,}50 \end{array} & \begin{array}{l} 0{,}40 \\ 0{,}40 \end{array} & \begin{array}{l} 0{,}40 \\ 0{,}40 \end{array} & \begin{array}{l} 0{,}31 \\ 0{,}50 \end{array} & \begin{array}{l} 0 \\ 1 \end{array} \end{array}$$

The places where x has here two equal values, are easily found from the value of x given in § 4. Evidently we must have then $\theta = (1-\omega)(2\omega - 1) = {}^1/_{12}$. This gives $\omega = 0{,}894$ and $0{,}606$, $= {}^1/_4\,(3 \pm {}^1/_3 \sqrt{3})$. For $\varphi = 1$ θ would have to be ${}^1/_4$, and there are no values of ω which satisfy this condition.

For the calculation of the different spinodal curves it is convenient to know the limiting values of τ again. We find for $x = 0$:

$$\begin{array}{llllllllll} v/b = 1/\omega = 1 & 1{,}25 & 1{,}50 & 1{,}75 & 2 & 2{,}25 & 2{,}50 & 2{,}75 & 3 \\ \tau = 0 & 0{,}51 & 1{,}19 & 1{,}68 & 2 & 2{,}20 & 2{,}30 & 2{,}36 & 2{,}37 \end{array}$$

For $x = 1$ these values are all $2^1/_4$ times greater.

For $x = {}^1/_2$ we find with the same values of ω:

$$\tau = 1 \quad 1{,}60 \quad 2{,}53 \quad 3{,}20 \quad 3{,}63 \quad 3{,}88 \quad 3{,}99 \quad 4{,}04 \quad 4{,}04$$

$\omega = 1$ yields the same values as in § 4 for $\varphi = 1$.

$\omega = {}^1/_3$ yields:

$x=$	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau=$	2,37	2,73	3,08	3,41	3,73	4,03	4,33	4,59	4,86	5,10	5,33

6. We may now determine, where the transition represented in fig. 4, takes place. (The place of the point P is also drawn in figs. 1 and 2 [1])).

If we put $1-\omega=y$ in the equation (2*b*) of the plaitpoint curve, then

$$(1-2x)+(x+\varphi)\,y^2\left(3+(x+\varphi)^2\frac{y\,(3y-2)}{x\,(1-x)}\right)=0. \quad . \quad . \quad . \quad (a)$$

Now in the double point sought $\frac{\partial f}{\partial x}$ must be 0 and $\frac{\partial f}{\partial y}$ must be 0, when f denotes the first member of (a). This gives:

$$-2x\,(1-x)+(1-2x)^2+3y^2\left\{(1-2x)\,(x+\varphi)+x\,(1-x)\right\}+$$
$$+3\,(x+\varphi)^2\,y^3\,(3y-2)=0\;, \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

and after division by $6y\,(x+\varphi)$:

$$x\,(1-x)+(x+\varphi)^2\,y\,(2y-1)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

Substitution of the value of $x\,(1-x)$ from (c) in (a) gives:

$$(1-2x)+(x+\varphi)\,y^2\left(3+\frac{3y-2}{1-2y}\right)=0,$$

or

$$(1-2x)+(x+\varphi)\,y^2\,\frac{1-3y}{1-2y}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a')$$

So we have to solve y, x and φ from (a'), (b) and (c). Substitution of $1-2x$ from (a'), and $x\,(1-x)$ from (c) in (b) gives, after division by $(x+\varphi)^2y$:

$$-2\,(1-2y)+y^3\left(\frac{1-3y}{1-2y}\right)^2+$$
$$+3y^2\left\{-y\,\frac{1-3y}{1-2y}+(1-2y)\right\}+3y^2\,(3y-2)=0,$$

i. e. after multiplication by $(1-2y)^2$:

$$-2\,(1-2y)^3+y^3\,(1-3y)^2+$$
$$+3y^2\,(1-2y)\left\{-y\,(1-3y)+(1-2y)^2\right\}+3y^2\,(3y-2)\,(1-2y)^2=0,$$

from which y may be solved. The above equation gives:

[1]) This point must be thought more to the left. In fig. 4 no contact but intersection takes place in the double point P.

$$-2(1-2y)^3+y^3(1-3y)^2+3y^2(1-2y)(y^2+2y-1)=0,$$

or
$$3y^5-15y^4+29y^3-27y^2+12y-2=0,$$

i. e. after division by $(y-1)^3$:
$$3y^2-6y+2,$$

yielding:
$$y=1\pm {}^1/_3\sqrt{3}.$$

As it is obvious that y cannot be larger than 1, only:
$$\underline{y=1-{}^1/_3\sqrt{3}=0{,}4226}$$

satisfies here.

If we substitute the value $x+\varphi$ from (a') into (c), we get:
$$x(1-x)-(1-2x)^2\frac{(1-2y)^3}{y^3(1-3y)^2}=0.$$

In this the last fraction passes into ${}^1/_4(1+\sqrt{3})$, after substitution of $y=1-{}^1/_3\sqrt{3}$, so that we get for x:
$$x(1-x)-{}^1/_4(1+\sqrt{3})\left\{1-4x(1-x)\right\}=0,$$

hence:
$$x(1-x)={}^1/_4(-1+\sqrt{3}),$$

giving:
$$x={}^1/_2\left\{1\pm{}^1/_2(\sqrt{6}-\sqrt{2})\right\}=0{,}2412 \text{ or } 0{,}7588.$$

It is obvious from the figure, that only the first value satisfies, viz.:
$$\underline{x={}^1/_2\left\{1-{}^1/_2(\sqrt{6}-\sqrt{2})\right\}=0{,}2412.}$$

The value of φ is finally found from (c):
$$(x+\varphi)^2=\frac{x(1-x)}{y(1-2y)}={}^3/_4(2+\sqrt{3}),$$

giving $x+\varphi={}^1/_4(3\sqrt{2}+\sqrt{6})$, hence $\underline{\varphi={}^1/_2(-1+\sqrt{2}+\sqrt{6})=1{,}432}$.

As $y=1-{}^1/_3\sqrt{3}$, $\omega={}^1/_3\sqrt{3}$, i.e. the intersection takes place at $v=b\sqrt{3}=1{,}732\,b$.

As mentioned before $T_0=T_1$ for $\varphi=1{,}30$ (see § 3). For $\varphi=1{,}43$ T_0 is already $<T_1$. For $T_1/T_0={}^{16}/_{27}\,\varphi^2$ we find easily the value 1,215, while 2,887 is found for $T_2/T_1=(1+1/\varphi)^2$.

7. Besides the cases, given in figs. 1 and 2, representing the principal types I and III, there is another important type, viz. II, of which I also gave a full description in my previous paper, which I have already cited several times [1]. The p,T-diagram of this case

[1] l. c. p. 663—667.

is given in fig. $4a$. KUENEN met with it, among others, in the case of mixtures of C_2H_6 with ethyl- and some higher alcohols. Also triethylamine with water is a well-known instance.

This case is evidently found, when the plaitpoint curve C_1C_2 of fig. 2 assumes the shape drawn in fig. 3. We may namely imagine that when the two curves C_1C_2 and C_0A approach each other, a deviation from the straight course may be found on the left side of C_1C_2, specially if b_1 should not be $= b_2$, by which the point C_0 would therefore be shifted to the left, to the side of the small volumes. At all events the anomaly of one of the two components can give rise to the occurrence of this second principal type, as I showed in a preceding paper.

From the shape of the different spinodal curves it is obvious that from C_1 the temperatures first increase, as far as the point of contact at R_1. The temperature is then T' (see fig. $3a$). But between R_1 and R_2', where the plaitpoint curve is again touched by one of the spinodal curves, the temperature *decreases*, and so also the pressure, so that in the p, T-diagram of fig. $3a$ the line $R_1\,R_2'$ *runs back* again, as in fig. $1a$ the line $R_1\,A$ and in fig. $2a$ the line $R_2\,A$, having in this case two *cusps* in R_1 and R_2'.

Here the points between R_1 and R_2', and also those on C_1R_1 and C_2R_2' in the neighbourhood of R_1 and R_2' can again not be realized, and the consequence will be the occurrence of a three phase equilibrium [1]).

As I already observed in one of my previous papers (l.c. p. 646), after the two liquid phases 1 and 2 have coincided in the neighbourhood of the point R'_2, here too, separation of the two liquid phases must take place again — provided the temperature be sufficiently lowered — and this will take place in the neighbourhood of the point, where one of the spinodal curves in R_2 touches the plaitpoint curve C_0A. This is also represented in the p, T-diagram of fig. $3a$.

When comparing figs. 1, 2 and 3, we see clearly the connection between the three principal types and their transition into each other. The connection is given by the different course of the two plaitpoint curves in figs. 1 and 2, which (see fig. 3) may pass *continuously* into each other with changed circumstances of critical data of the two components.

1) Cf. VAN DER WAALS, Continuität II, p. 187, and These Proceedings V, p. 307—11 Oct. 25, 1902.

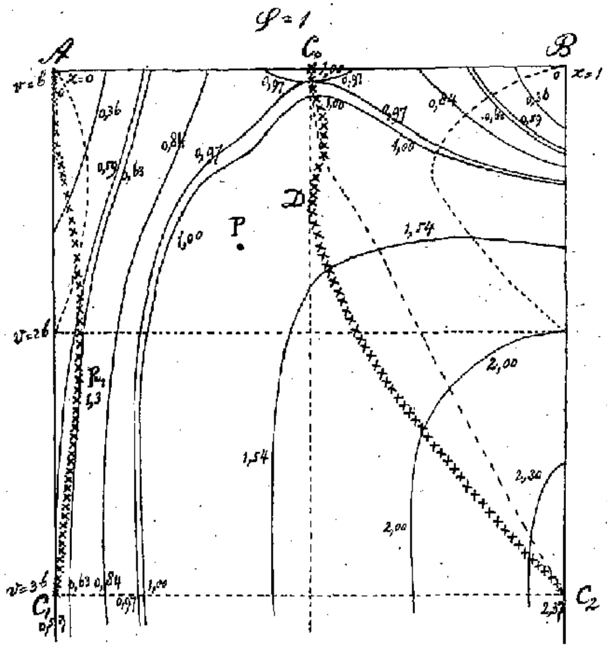

Fig. 1.

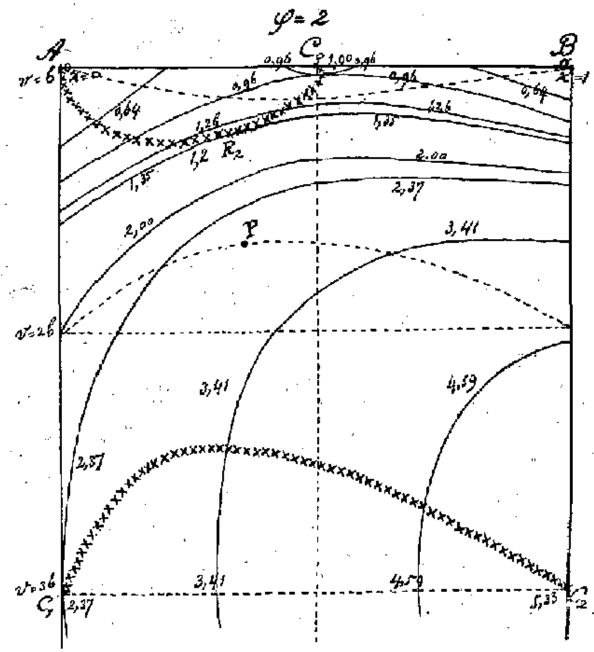

Fig. 2.

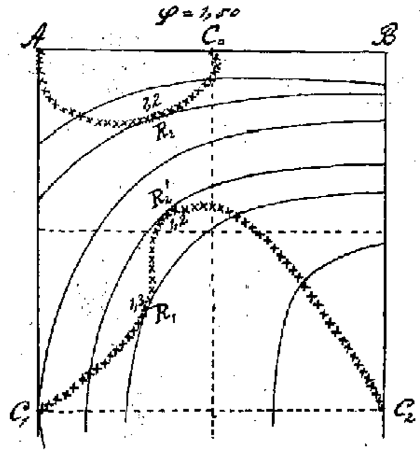

Fig. 3.

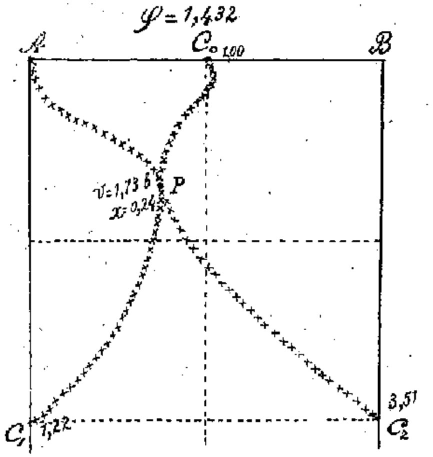

Fig. 4.

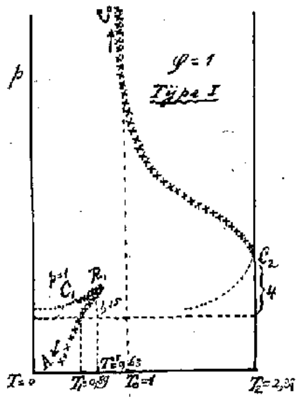

Fig. 1a.

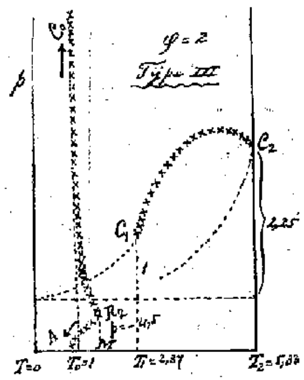

Fig. 2a.

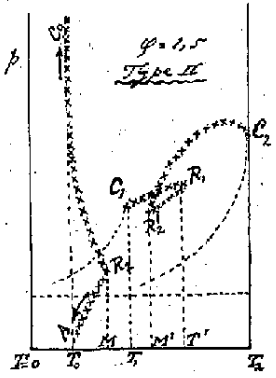

Fig. 3a.