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9. Now, that we have sufficiently characterised the three general types, and have brought some harmony into the multiplicity of the phenomena, the question arises, whether there is a still farther synthesis, a still higher unity. More than once the occasion presented itself in the treatment of the different general types to remark striking agreements and continuous transitions, often accompanied with great differences. Equally the fact, that with a higher alcohol or a higher hydrocarbon, suddenly a quite different type often appears, must certainly draw attention in a high degree. All this induces us to look for the *one* fundamental type, of which the three types, treated above, are special cases.
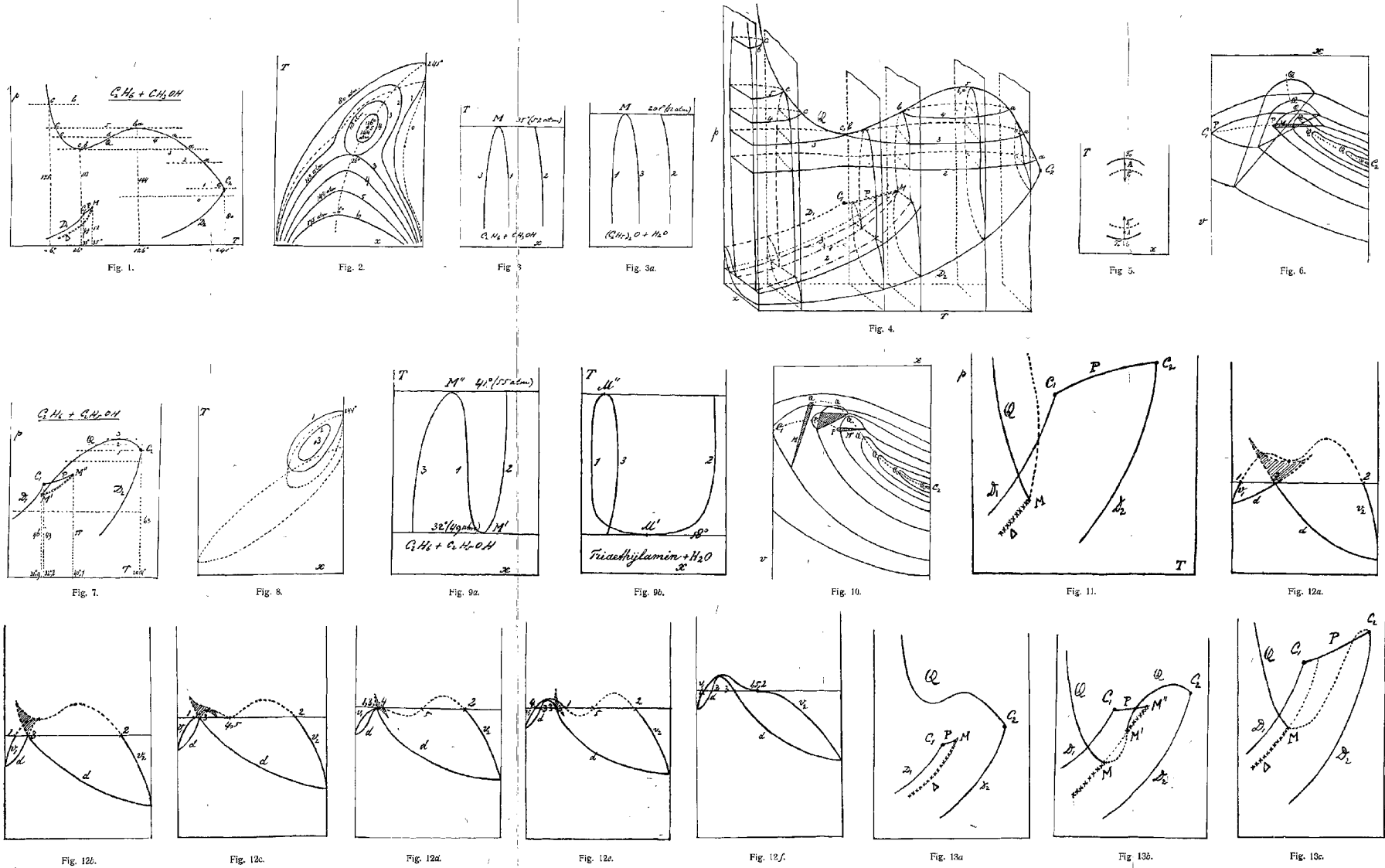
Also the *analytical* consideration of the question suggests that idea to us. Indeed, the coexistence of two liquid phases and one gaseous phase, or of two liquid phases, or finally of one liquid phase and one gaseous phase, is determined by one and the same equation of state, and it must consequently always be possible to reduce all the different cases, which may occur to *two* fundamental proportions: that of the *critical temperatures* and that of the *critical pressures* of the two components — entirely in the same way as I have formerly deduced *all* the different types in the case of mixed crystals, where appear two solid phases by the side of one liquid phase, from *two* fundamental proportions: that of the *meltingtemperatures* and that of the *latent heats of melting* of the two components.

In a following communication it will be shown theoretically, that the three types may be deduced from the ordinary equation of state of Prof. van der Waals, even in the case of *normal* components. In connexion with this we must not forget, that in the neighbourhood of the critical points of each of the components the influence of anomaly vanishes nearly always. In the case of $C_2H_6 + H_2O$ for instance the water will be in the neighbourhood of 365° C. already normal long before, and in the neighbourhood of 32° C. the liquid phase, which consists nearly entirely of ethane, will contain the water in such a dilute state, that this will be passed for the greater part into the state of simple molecules.

Chemistry. — *"An exact expression for the course of the spinodal curves and of their plaitpoints for all temperatures, in the case of mixtures of normal substances."* By J. J. van Laar. (Communicated by Prof H. A. Lorentz).

(Communicated in the meeting of March 25, 1905.)

1. It is well-known, that the points of the ζ-surface, corresponding to points of the spinodal curve on the ψ-surface, are given by the simple relation

Fig. 1.

Fig. 2.

Fig 3.

Fig. 3a.

Fig. 4.

Fig 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9a.

Fig. 9b.

Fig. 10.

Fig. 11.

Fig. 12a.

Fig. 12b.

Fig. 12c.

Fig. 12d.

Fig. 12e.

Fig. 12f.

Fig. 13a.

Fig. 13b.

Fig. 13c.

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$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T} = 0,$$

which corresponds with the condition $\dfrac{\partial^2 \psi}{\partial x^2} \dfrac{\partial^2 \psi}{\partial v^2} - \left(\dfrac{\partial^2 \psi}{\partial x \partial v}\right)^2 = 0,$[1]) when instead of the thermodynamic potential the free energy is used, and not x, p and T, but x, v and T are the independent variables.

As we have further in the case of normal components e. g.

$$\mu_1 = \frac{\partial \zeta}{\partial n_1} = \zeta - x \frac{\partial \zeta}{\partial x},$$

we have also $\dfrac{\partial \mu_1}{\partial x} = - x \dfrac{\partial^2 \zeta}{\partial x^2}$, and the above-mentioned condition may be replaced by

$$\frac{\partial \mu_1}{\partial x} = 0.$$

Now

$$\mu_1 = C_1 - \left(\omega - x \frac{\partial \omega}{\partial x}\right) + RT \, log \, (1 - x),$$

where C_1 is a pure function of the temperature, whereas ω is given by

$$\omega = \int p dv - pv.$$

The condition $\dfrac{\partial \mu_1}{\partial x} = 0$ is therefore identical with

$$x \frac{\partial^2 \omega}{\partial x^2} - \frac{RT}{1-x} = 0,$$

or

$$RT = x \, (1 - x) \frac{\partial^2 \omega}{\partial x^2}, \quad \cdots \cdots \cdots \quad (1)$$

from which I also started in my preceding communication[2]).

Now the difficulty arises, that the exact calculation of $\dfrac{\partial^2 \omega}{\partial x^2}$ leads to rather complicated expressions, so that VAN DER WAALS contented himself most times with approximations. These consisted in this, that in the liquid state at sufficiently low temperatures 1st p was omitted by the side of $\dfrac{a}{v^2}$, 2nd terms of order $v - b$ were neglected against those of order v.

Starting namely from the equation of state of VAN DER WAALS

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[1]) Compare VAN DER WAALS, Cont. II, p. 137.

[2]) These Proc. 28 Jan. 1905.

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where b will be regarded as *independent* of v and T, then we find for ω:

$$\omega = RT \log (v - b) + \frac{a}{v} - pv \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we write now $\dfrac{RT}{p + a/v^2}$ for $v - b$, and omit p, then we obtain:

$$\frac{\partial \omega}{\partial x} = - RT \frac{\partial}{\partial x} \log \frac{a}{v^2} + \frac{\partial}{\partial x}\left(\frac{a}{v}\right),$$

in which VAN DER WAALS further wrote b for v, whereas for illustrating several properties $\dfrac{a}{b}$ was brought in connexion with T_x, and $\dfrac{a}{b^2}$ with p_x.

This is consequently a complete set of approximations, and with good reason Prof. LORENTZ remarked to me, that in such cases we must be carefull, whether these approximations are not in contradiction, and up to what temperatures the results, deduced with the above-mentioned expression for $\dfrac{\partial \omega}{\partial x}$, can be used.

VAN DER WAALS himself considered therefore the deduced expression merely as a more or less rough approximation, but which is at all events better than the former expression $\dfrac{\partial \omega}{\partial x} = \dfrac{\partial}{\partial x}\left(\dfrac{a}{v}\right) = \dfrac{\partial}{\partial x}\left(\dfrac{a}{b}\right)$, where the term with $\dfrac{\partial}{\partial x} \log \dfrac{a}{v^2}$ was omitted.

Now, I showed in my preceding communication, that at *low* temperatures, and in the case of *normal* substances, where the critical pressures rarely differ much, this omitted term has in the greater part of cases a very small value, and is of *entirely the same* order as $\dfrac{v - b}{v}$, which is constantly neglected.

Only at higher temperatures the term has a large value, but then the deduced expression for $\dfrac{\partial \omega}{\partial x}$ is not exact enough by far, for then neither p can be neglected against $\dfrac{a}{v^2}$, nor terms of order $\dfrac{v - b}{b}$ can be omitted in that case.

The matter is consequently this: at sufficiently low temperatures

the former simple expression $\frac{\partial \omega}{\partial x} = \frac{\partial}{\partial x}\left(\frac{a}{b}\right)$ may be safely used, at least in the case of normal substances; but at higher temperatures equally the new expression with the term $\frac{\partial}{\partial x} \log \frac{a}{v^2}$ will be insufficient.

And we want a more accurate expression for $\frac{\partial \omega}{\partial x}$ and $\frac{\partial^2 \omega}{\partial x^2}$ the more, when we — specially with respect to the course of the plait-point-curve — also wish to know anything about the course of the spinodal curves from the lowest temperatures to the highest critical temperature.

I therefore tried to solve that problem; I was the more encouraged to do so, as soon it appeared to me, that the entirely accurate expressions are not so complicated as was expected. On the contrary, the often occurring fact presented itself here, that the exact expression is relatively more simply than the approximated one.

2. If we write the equation (2) in the form

$$\omega = \frac{a}{v} + RT \log (v-b) - p (v-b) - pb,$$

then we obtain:

$$\frac{\partial \omega}{\partial x} = \frac{\partial}{\partial x}\left(\frac{a}{v}\right) + \left(\frac{RT}{v-b} - p\right)\frac{\partial(v-b)}{\partial x} - p\frac{db}{dx}.$$

Now $\frac{RT}{v-b} - p = \frac{a}{v^2}$, consequently we find further:

$$\frac{\partial \omega}{\partial x} = \frac{1}{v}\frac{da}{dx} - \frac{a}{v^2}\frac{\partial v}{\partial x} + \frac{a}{v^2}\frac{\partial v}{\partial x} - \frac{a}{v^2}\frac{db}{dx} - p\frac{db}{dx},$$

or

$$\frac{\partial \omega}{\partial x} = \frac{1}{v}\frac{da}{dx} - \left(p + \frac{a}{v^2}\right)\frac{db}{dx}, \quad \ldots \ldots \quad (3)$$

where $\frac{\partial v}{\partial x}$ appears no more.

If we write now:

$$a = (1-x)^2 a_1 + 2x(1-x) a_{12} + x^2 a_2,$$

and if we put $a_{12} = \sqrt{a_1 a_2}$, by which the calculations and the results are simplified in some way, without affecting much the exactness of these results [1]), then we have:

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[1]) I am convinced, that the expression $a_{12} = \sqrt{a_1 a_2}$ is exact in the case of normal substances. At all events the inaccuracy, which results from this supposition, will certainly not be greater than that of the equation of state used.

$$a = ((1-x)\sqrt{a_1} + x\sqrt{a_2})^2.$$

Further we admit for b the ordinary linear relation

$$b = (1-x) b_1 + x b_2 .$$

The suppositions, on which the following calculations are based, are consequently the following.

1st. the equation of state of VAN DER WAALS, with b independent of v and T.

2nd. the ordinary suppositions about a and b.

3rd. the special supposition $a_{12} = \sqrt{a_1 a_2}$.

From the expressions for a and b used results:

$$\frac{da}{dx} = 2\left((1 - x)\sqrt{a_1} + x\sqrt{a_2}\right)(\sqrt{a_2} - \sqrt{a_1}) = 2\sqrt{a} . (\sqrt{a_2} - \sqrt{a_1})$$

$$\frac{d^2 a}{dx^2} = 2(\sqrt{a_2} - \sqrt{a_1})^2$$

$$\frac{db}{dx} = b_2 - b_1 \quad ; \quad \frac{d^2 b}{dx^2} = 0.$$

If we did not put $a_{12} = \sqrt{a_1 a_2}$, then we should have found $\frac{d^2 a}{dx^2} = 2(a_1 + a_2 - 2a_{12})$. so only somewhat less simple.

3. We will now calculate $\frac{\partial^2 \omega}{\partial x^2}$.

For (3) we can write:

$$\frac{\partial \omega}{\partial x} = \frac{2\sqrt{a}}{v}(\sqrt{a_2} - \sqrt{a_1}) - \left(p + \frac{a}{v^2}\right)(b_2 - b_1),$$

so that we obtain, when for shortness' sake α is written for $\sqrt{a_2} - \sqrt{a_1}$, and β for $b_2 - b_1$:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{2}{v}(\sqrt{a_2} - \sqrt{a_1})^2 - \frac{2\sqrt{a}}{v^2}(\sqrt{a_2} - \sqrt{a_1})\frac{\partial v}{\partial x} -$$

$$- (b_2 - b_1)\left\{\frac{2\sqrt{a}}{v^2}(\sqrt{a_2} - \sqrt{a_1}) - \frac{2a}{v^3}\frac{\partial v}{\partial x}\right\} =$$

$$= \frac{2\alpha^2}{v} - \frac{2\alpha\beta\sqrt{a}}{v^3} + \left(\frac{2\alpha\beta}{v^3} - \frac{2\alpha\sqrt{a}}{v^2}\right)\frac{\partial v}{\partial x}$$

$$= \frac{2}{v}\left\{\alpha^2 - \alpha\beta\frac{\sqrt{a}}{v} + \frac{\sqrt{a}}{v}\left(\beta\frac{\sqrt{a}}{v} - \alpha\right)\frac{\partial v}{\partial x}\right\}.$$

Consequently we must calculate $\frac{\partial v}{\partial x}$.

From the equation of state $\left(p + \dfrac{a}{v^2}\right)(v - b) = RT$ we deduce:

$$\left(p + \frac{a}{v^2}\right)\left(\frac{\partial v}{\partial x} - \frac{db}{dx}\right) + (v - b)\left(\frac{1}{v^2}\frac{da}{dx} - \frac{2a}{v^3}\frac{\partial v}{\partial x}\right) = 0,$$

yielding

$$\frac{\partial v}{\partial x} = \frac{\left(p + \dfrac{a}{v^2}\right)\dfrac{db}{dx} - \dfrac{v - b}{v^2}\dfrac{da}{dx}}{p + \dfrac{a}{v^2} - \dfrac{2a\,(v - b)}{v^3}},$$

or also

$$\frac{\partial v}{\partial x} = \frac{\dfrac{db}{dx} - \dfrac{1}{RT}\dfrac{(v - b)^2}{v^2}\dfrac{da}{dx}}{1 - \dfrac{2a/v}{RT}\dfrac{(v - b)^2}{v^2}} \quad \ldots \ldots \ldots \quad (4)$$

Substituting this in the last equation for $\dfrac{\partial^2 \omega}{\partial x^2}$, we obtain:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{2}{v}\left[\left(a^2 - a\beta\frac{\sqrt{a}}{v}\right)\left\{1 - \frac{2a/v}{RT}\frac{(v - b)^2}{v^2}\right\} + \right.$$

$$\left. + \frac{\sqrt{a}}{v}\left(\beta\frac{\sqrt{a}}{v} - a\right)\left(\beta - \frac{2a\sqrt{a}}{RT}\frac{(v - b^2)}{v^2}\right)\right] : \left(1 - \frac{2a/v}{RT}\frac{(v - b)^2}{v^2}\right),$$

since $\dfrac{da}{dx} = 2a\sqrt{a}$ and $\dfrac{db}{dx} = \beta$. Further treatment yields after important simplification:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{2}{v}\frac{\left(a - \beta\dfrac{\sqrt{a}}{v}\right)^2}{1 - \dfrac{2a/v\,(v - b)^2}{RT}\dfrac{}{v^2}} \quad \ldots \ldots \ldots \quad (5)$$

Comparing this entirely exact expression with that, deduced in my former communication, where p and $\dfrac{v - b}{v}$ were neglected, we see that the exact expression (5) is already simpler than the approximated one, which may easily be written down by means of the expressions for $\dfrac{\partial^2}{\partial x^2}\left(\dfrac{a}{v}\right)$ and $\dfrac{\partial^2}{\partial x^2} \log \dfrac{a}{v^2}$, deduced there.

4. Consequently equation (4) passes into

$$RT = \frac{2x\,(1 - x)}{v^3}\frac{(av - \beta\sqrt{a})^2}{1 - \dfrac{2a/v\,(v - b)^2}{RT}\dfrac{}{v^2}},$$

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that is to say into

$$RT - 2\,\frac{a}{v}\,\frac{(v-b)^2}{v^2} = \frac{2x\,(1-x)}{v^3}\,(av - \beta\sqrt{a})^2\,,$$

or into

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

Now $av - \beta\sqrt{a} = a\,(v-b) + ab - \beta\sqrt{a}$

$$= a\,(v-b) + a\,(b_1 + x\beta) - \beta\,(\sqrt{a_1} + x a)$$

$$= a(v-b) + (ab_1 - \beta\sqrt{a_1}) = a(v-b) + (b_1\sqrt{a_2} - b_2\sqrt{a_1}).$$

Therefore we obtain (compare also van der Waals, Cont. II, p. 45):

$$RT = \frac{2}{v^3}\left[\,x(1-x)\left\{(b_1\sqrt{a_2} - b_2\sqrt{a_1}) + a(v-b)\right\}^2 + a(v-b)^2\,\right],\;\ldots(6)$$

being, with the above mentioned suppositions, the sought, quite general expression for $T = f(v,x)$, by which for each given temperature the v, x-projection of the spinodal curve is entirely determined. We may also construct a "spinodal surface" $T = f(v, x)$, and immediately deduce from the subsequent sections $T = $ const. the forms of the spinodal curves of the transversal- and longitudinal plaits, and this in just the same v, x-representation as is used by van der Waals for the projection of the spinodal curves of the surfaces $\psi = f(T,v,x)$ for different values of T.

5. The equation (6) gives rise to some results, which may be deduced from it without further calculation.

1st. Is $v = b$, that is to say, is the limit of volume b_x reached at any value of x, then (6) reduces to the equation of the boundary-curve, lying in the v, x-plane:

$$RT = \frac{2}{b^3}\,x\,(1-x)\,(b_1\sqrt{a_2} - b_2\sqrt{a_1})^2,\;\ldots\ldots(6a)$$

viz. the same expression, which was formerly found for small values of v by means of the approximating method.

It is obvious at present, that only for $v = b$ the expression $(6a)$ holds rigorously good. In every other case terms with $v-b$ must be added. But it also results from the found expression (6), that as long as terms with $v-b$ may be neglected, the formula (6^1) gives approximately the projection of the spinodal curve on the T, x-plane, without it being necessary to take into account the corrective-term with $\frac{\partial^2}{\partial x^2}\,log\,\frac{a}{b^2}$, indicated by van der Waals. In a former communication

I showed already, that this correction-term is small in the case of *normal* substances, about of order $v - b$.

As the second member of the expression (6^a) is always *positive*, even when a_{12} should be $< \sqrt{a_1 a_2}$, the *longitudinal* plait on the ψ-surface (for it is obvious, that in the neighbourhood of $v = b$ the spinodal curve belongs to the longitudinal plait, which can be regarded as a prominence of the transversal plait) will *always* close itself above a definite temperature at the side of the small volumes.

This temperature T_0 is the plaitpoint-temperature, corresponding to (6^a); it is given by (6^a), in connexion with the expression for $\dfrac{dT}{dx} = 0$, deduced from it, yielding for the plaitpoint after elimination of T the value

$$ x_c = \frac{1}{r} \left[(r + 1) - \sqrt{r^2 + r + 1} \right], $$

where $r = \dfrac{b_2 - b_1}{b_1}$. (compare VAN DER WAALS, Cont. II, and also my preceding communication, p. 579). Only when $b_2 = b_1$ ($r = 0$), x_c will be $= \frac{1}{2}$. In each other case x_c will be removed to the side of the smallest molecular volume.

Just *at* T_0 the closing will take place at the limit of volume $v = b$ ($x = x_c$); for values of $T < T_0$ the longitudinal plait will remain *unclosed* up to the smallest volumes. For in that case (compare the representation in space) a section T=const. will cut the boundary-curve (6^a), lying in the boundary-plane $v = b$, in a straight line.

This temperature T_0 may consequently be regarded in any respect as a *third* critical temperature. For *above* that temperature *a formation of two liquid layers* will never present itself at values of v in the neighbourhood of b, that is to say at very high pressures; just in the same manner as *above* the ordinary critical temperatures of the single substances can never appear a liquid phase in presence of a gaseous one.

2nd. Is $v = \infty$, then for each value of x, T will be $= 0$, that is to say, the equation (6) cannot be satisfied in that case. The plait will consequently never extend to $v = \infty$.

3rd. Is $x = 0$ or 1, then (6) passes into the two boundary-curves, lying in the two limiting T, v-planes, viz.

$$ RT = \frac{2a_1}{v^3} (v - b_1)^2 \quad \text{and} \quad RT = \frac{2a_2}{v^3} (v - b_2)^2. $$
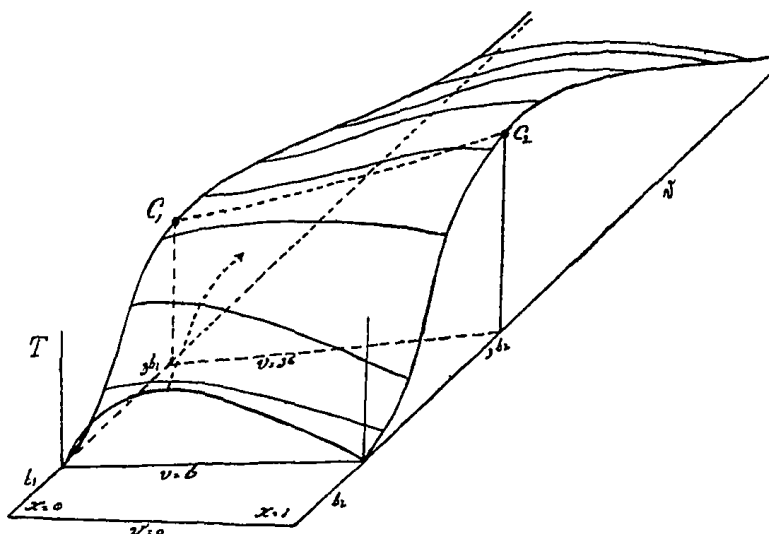
With $v = 3 b_1$ (resp. $3b_2$) these two curves yield duly:

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$$RT_1 = \frac{8}{27}\frac{a_1}{b_1} \quad ; \quad RT_2 = \frac{8}{27}\frac{a_2}{b_2}, \quad . \quad , \quad . \quad . \quad . \quad (6^b)$$

which is again a good test of the exactness of our formula, deduced above.

These two critical points are at the same time plaitpoints of the (transversal) plait, for it can easily be shown, that $\left(\frac{\partial T}{\partial v}\right)_x$, and also $\left(\frac{\partial T}{\partial x}\right)_p$ will be there $= 0$.

Before deducing the equation of the plaitpoint-curve, I shall first point out, that the second member of (6) is *always positive*, as consisting of the sum of two essential positive terms, so that the T, v, x-surface possesses nowhere points beneath the v, x-plane, which of course cannot occur, because T cannot be negative. Further, that from (6^a) and (6^b) results, that as to the limiting-curve (6^a), there will be found $T = 0$ for $x = 0$ and $x = 1$, and as to the limiting-curves (6^b), T assumes again the value 0, as well for $v = b_1$ (resp. b_2), as for $v = \infty$.

Since the values of T_2/T_1 and b_2/b_1 can be very different, according to different substances, the surface (6) will also present very different forms. Generally a greater value of b corresponds with a greater value of T_c, and in that case the surface has the form, as is indicated in the figure. It is manifest already at superficial consideration, that this form will be pretty complicated.

6. We will now determine from (6) the locus of the plaitpoints.

This may be found by combination of the two conditions

$$\left(\frac{\partial \mu_1}{\partial x}\right)_{p,T} = 0 \quad ; \quad \left(\frac{\partial^2 \mu_1}{\partial x^2}\right)_{p,T} = 0,$$

leading to

$$\frac{\partial f}{\partial x} + \frac{\partial f}{\partial v}\left(\frac{\partial v}{\partial x}\right)_{p,T} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

when f represents the second member of (6). Indeed, this second member has in all points of the spinodal curve on the ψ-surface the same value, so that we have, by passing along an element of that curve:

$$\frac{\partial f}{\partial x}\,dx + \frac{\partial f}{\partial v}\,dv = 0 \,.$$

But in the plaitpoint we may regard an element of the spinodal curve also as an element of the connodal curve, that is to say as the line which joins the two tangent-points of a double tangent-plane, when the tangent-points have approached each other to an infinitely small distance. And as in these two tangent-points the pressure has the same value, the latter does not vary, when at the plaitpoint we pass along the considered element of the spinodal curve. Consequently we have:

$$dv = \left(\frac{\partial v}{\partial x}\right)_{p,T}\,dx,$$

which yields immediately equation (7).

For shortness, we will write in the following $b_1\sqrt{a_2} - b_2\sqrt{a_1} = \pi$, by which the second member of (6) passes into

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

The value of $\left(\frac{\partial v}{\partial x}\right)_{p,T}$ will be found from (4), viz.

$$\left(\frac{\partial v}{\partial x}\right)_{p,T} = \frac{\beta - \dfrac{2a\sqrt{a}}{RT}\dfrac{(v-b)^2}{v^2}}{1 - \dfrac{2\,a/_v}{RT}\dfrac{(v-b)^2}{v^2}} \,.$$

And since the denominator of this expression cannot become ∞, (7) passes into

$$\left(1 - \frac{2\,a/_v}{RT}\frac{(v-b)^2}{v^2}\right)\frac{\partial f}{\partial x} + \left(\beta - \frac{2a\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right)\frac{\partial f}{\partial v} = 0. \quad \cdot \quad (7a)$$

Now we have:

$$\tfrac{1}{2}v^3 \frac{\partial f}{\partial x} = \theta^2(1-2x)-2x(1-x)\theta\alpha\beta-2a(v-b)\beta+2a\sqrt{a}(v-b)^2$$

$$\tfrac{1}{2}v^3 \frac{\partial f}{\partial v} = \qquad\qquad 2x(1-x)\theta\alpha + 2a(v-b) \qquad\qquad -\frac{3\varphi}{v} \Bigg\},$$

where θ is written for $\pi + a(v-b)$, and φ for $\tfrac{1}{2}v^3 f$.

The equation (7a) becomes consequently:

$$\left\{1-\frac{2a/v}{RT}\frac{(v\ b)^2}{v^2}\right\}\left\{\theta^2(1-2x)+2a\sqrt{a}(v-b)^2\right\}-\left\{\beta-\frac{2a\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\}\frac{3\varphi}{v}+$$

$$+2\left\{x.(1-x)\theta\alpha+a(v-b)\right\}\left[\left\{\beta-\frac{2a\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\}-\beta\left\{1-\frac{2a/v}{RT}\frac{(v-b)^2}{v^2}\right\}\right]=0.$$

The expression between [ ] is obviously:

$$-\frac{2\sqrt{a}/v}{RT}\frac{(v-b)^2}{v^2}(\alpha v-\beta\sqrt{a})=-\frac{2\sqrt{a}/v}{RT}\frac{(v-b)^2}{v^2}\theta,$$

as $\alpha v - \beta\sqrt{a} = \pi + a(v-b) = \theta$. Further we have $RT = \frac{2\varphi}{v^3}$, in consequence of (6), so that we obtain:

$$\left\{1-\frac{a(v-b)^2}{\varphi}\right\}\left\{\theta^2(1-2x)+2a\sqrt{a}(v-b)^2\right\}-\left\{\beta-\frac{a\sqrt{a}\,v(v-b)^2}{\varphi}\right\}\frac{3\varphi}{v}-$$

$$-\frac{2\theta\sqrt{a}\,(v-b)^2}{\varphi}\left\{x(1-x)\theta\alpha+a(v-b)\right\}=0.$$

And since $\varphi - a(v-b)^2 = x(1-x)\theta^2$, we have, after multiplication with φ:

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

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

In this expression the underlined terms vanish. And for $\beta\varphi - a\sqrt{a}.v(v-b)^2$ may be written:

$$\beta x(1-x)\theta^2-\sqrt{a}(v-b)^2(\alpha v-\beta\sqrt{a})=\beta x(1-x)\theta^2-\sqrt{a}(v-b)^2\theta,$$

so that we obtain, after dividing by θ, and multiplying by v:

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

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

or finally:

$$\left| x(1-x)\theta^3 \left[(1-2x)v - 3x(1-x)\beta \right] + \sqrt{a}(v-b)^2 \left[3x(1-x)\theta(\theta-\beta\sqrt{a}) + \right.\right.$$
$$\left. + a(v-b)(v-3b) \right] = 0, \quad . \quad . \quad . \quad (8)$$

where $\theta - \beta\sqrt{a}$ may be substituted by $av - 2\beta\sqrt{a}$.

This is consequently the sought equation of the v, x-projection of the locus of all the plaitpoints, which can appear on the ψ-surfaces at different values of T. Combined with (6), we find the points of the surface, represented by (6), which satisfy the plaitpoint-condition, that is to say the equation of the plaitpoint-curve as space-curve. Equation (6) may be written:

$$RT = \frac{2}{v^3}\left[x(1-x)\theta^2 + a(v-b)^2 \right], \quad . \quad . \quad (6)$$

where thus $\theta = \pi + a(v-b)$, and $\pi = b_1\sqrt{a_2} - b_2\sqrt{a_1}$.

For $v = b$ (8) passes into

$$(1 - 2x)b - 3x(1-x)\beta = 0,$$

yielding $x_c = \frac{1}{r}\left[(r+1) - \sqrt{r^2 + r + 1} \right]$, as we have deduced already above (in § 5) for that limiting-case.

To conclude, we remark, that the sections for constant volume of the surface, given by (6), *only* extend down to $T = 0$ ($x = 0$ and 1) for $v = b$. For all volumes $> b$, T will assume for $x = 0$ and 1, as is obvious from (6), a *finite* value, viz. $\dfrac{2a(v-b)^2}{v^3}$. The T,x-boundary-curve suddenly ends then at the T-axis at the designed value of T (also compare the space-representation).

The proper discussion of the equations (6) and (8) must be reserved for a separate communication. It will appear then, that the different forms of the spinodal- and plaitpoint-curves, which occur specially in the case of anomalous substances, are already possible in the case of *normal* substances, provided the proportion of the two critical temperatures T_2/T_1 be sufficiently large. The spinodal curves, given by (6), will appear easily calculable, and as to the course of the plaitpoint-curve (there are two, independent of each other), some conclusions will be deduced in a simple way.

It will also appear, which indeed results already from (6), that the longitudinal- and the transversal plaits — at least with respect to the *spinodal* curves (compare also VAN DER WAALS, Cont. II, p. 175) — are no separate plaits, but *one* single plait, of which the plaitpoint is lying, according to the different circumstances, either on the side of the small volumes, or somewhere else.