

Physics. — Dr. J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS' ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components." (Continued). Communication n^o. 81 from the physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. ¹⁾

(Communicated in the meeting of Sept. 27, 1902).

10. The border curve and the connodal line in special cases.

1. When $m_{01} = 0$, i. e. $p_k \beta = k_{01} T_k a$, all isotherms intersect one another nearly at the critical point (p_{Tk}, v_{Tk}) as we have seen in § 3; according to the equations (26), (27) and (28) the plaitpoint coincides in that case with this critical point. Besides from (31) it follows that $\frac{d^2 p}{dv^2} = 0$; this value however belongs to $\frac{d^2 p}{dv^2}$ only to the first approximation (i. e. at the critical point itself), or the border curve is a parabola of a higher degree than the second. In fact we find in this case:

$$\Phi = -\frac{1}{2m_{30}} \left(\frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{11} m_{40}}{m_{30}} \right) \Xi^3, \quad \varphi^2 = -\frac{m_{11}}{m_{30}} \Xi^2, \text{ and}$$

$$p_1 - p_{Tk} = \left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} \right) \Xi^2;$$

and therefore the border curve to the first approximation becomes a parabola of the fourth degree; the equation of that parabola is:

$$p - p_{Tk} = \frac{m_{30}^2}{m_{11}^2} \left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} \right) (v - v_{Tk})^4.$$

The connodal line, however, remains a parabola of the second degree, on which $\frac{d^2 x}{dv^2} = \frac{2k_{30}}{T_k k_{11} a}$.

2. A second remarkable case is that where $RT_k m_{11} + m_{01}^2 = 0$; for then the term $p_1 - p_{Tk}$ disappears from the expression for φ^2 (equation 23), so that φ becomes of the first order with respect to $p_1 - p_{Tk}$. We then find:

$$\Phi = -\frac{1}{3m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \frac{p_1 - p_{Tk}}{m_{01}} - \frac{m_{01}}{RT_k m_{30}} \left(\frac{1}{3} m_{11} - \frac{2}{5} \frac{m_{01} m_{40}}{m_{30}} \right) x_{Tk}$$

and

$$\varphi^2 = \frac{m_{11} x_{Tk}}{m_{30}} - \frac{1}{m_{30}} \left(\frac{5}{2} \frac{m_{01} m_{02}}{RT_k} - \frac{1}{3} \frac{m_{01}^2 m_{11}^2}{R^2 T_k^2 m_{30}} + m_{11} + m_{12} - \frac{2}{3} \frac{m_{01} m_{11} m_{21}}{RT_k m_{30}} - \frac{1}{3} \frac{m_{21}^2}{m_{30}} \right) \left(\frac{p_1 - p_{Tk}}{m_{01}} \right)^2;$$

¹⁾ Comp. Proceedings Royal Acad. of Sciences Sept. 1902.

in the last term I shall express the co-efficient of $(p_1 - p_{T_k})^2$ for convenience by K .

Substituting this in equation (30) we obtain to the first approximation an equation of the second degree, which now no longer represents a parabola but an ellipse or a hyperbola. The coordinates of the centre are:

$$p_c = p_{T_k} \quad \text{and} \quad v_c = v_{T_k} - \frac{m_{01}}{RT_k m_{30}} \left(\frac{1}{3} m_{11} - \frac{2}{5} \frac{m_{01} m_{40}}{m_{30}} \right) x_{T_k},$$

while the straight lines

$$p = p_{T_k} \quad \text{and} \quad v = v_{T_k} + \Phi$$

are conjugate axes. With respect to these axes the coordinates of the border curve are φ and $p_1 - p_{T_k}$, so that the equation of the border curve with respect to those axes is:

$$\varphi^2 - K(p - p_{T_k})^2 = \frac{m_{11}}{m_{30}} x_{T_k} = - \frac{k_{11}}{k_{30}} (T - T_k).$$

In the same case the equation of the connodal line is:

$$\varphi'^2 - K m_{01}^2 (x - x_{T_k})^2 = - \frac{k_{11}}{k_{30}} (T - T_k),$$

with respect to the conjugate axes:

$$x = x_{T_k} \quad \text{and} \quad v = v_{T_k} + \Phi';$$

where Φ' is obtained through substituting $x - x_{T_k}$ for $\frac{p_1 - p_{T_k}}{m_{01}}$ in Φ .

We must now distinguish two cases.

a. $K < 0$; the equations of the border curve and the connodal line represent ellipses. Provided $k_{11} < 0$ and $k_{30} < 0$ these ellipses are real when $T < T_k$; they lie only partially — to the first approximation half — in the real part ($v > 0$) of the ψ -surface. We find two plaitpoints of which only one is in the real ψ -surface and two critical points of contact co-inciding with the plaitpoints (at least to the degree of approximation considered here, i. e. to the order $\sqrt{T - T_k}$); the coordinates of these points are:

$$x_{T_p l} = x_{T_r} = x_{T_k} \pm \frac{1}{m_{01}} \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}$$

$$p_{T_p l} = p_{T_r} = p_{T_k} \pm \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}$$

$$v_{T_p l} = v_{T_r} = v_c \mp \frac{1}{3 m_{01} m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}.$$

If $T = T_k$, the border curve and the connodal line shrink to one point, the critical point of the pure substance; and if $T > T_k$, there is no longer a border curve nor a connodal line.

b. $K > 0$; the border curve and the connodal line are hyperbolae; the asymptotes are:

$$\varphi = \pm(p - p_{Tk}) \sqrt{K} \text{ (border curve) and } \varphi' = \pm m_{01}(x - x_{Tk}) \sqrt{K} \text{ (connodal line).}$$

If $T > T_k$, φ (or φ') is the real axis; only that branch of the hyperbola which lies above the axis $p = p_{Tk}$ can be observed as border curve; in the case of the connodal line it is only the branch lying above the axis $x = x_{Tk}$ which can be observed; again two plaitpoints are found of which only one can be observed, and the coordinates of which can be expressed by the same terms as used for the ellipse. If $T = T_k$, the border curve and the connodal line consist of two straight branches meeting at the critical point of the pure substance, which is therefore a double plaitpoint. Lastly, if $T < T_k$ there is no longer a plaitpoint; we observe two branches of the border curve and the connodal line lying to the right and the left of the point p_{Tk} , v_{Tk} ; each phase on one branch co-exists with a phase on the other.

11. *The border curve in the p, v, T diagram for a mixture of composition x .*

In equation (36) of the projection of the connodal line on the x, v -plane, if we consider x as constant and T as variable, that equation will express how the volumes of the phases, where the condensation begins and ends depend for the same mixture on the temperature. It therefore may be considered as the projection on the v, T -plane of the border curve on the p, v, T -surface for the mixture of composition x .

This projection, can be written in the following form, corresponds to (36)

$$0 = (v - v_{xk})^2 - 2 \Phi'' (v - v_{xk}) + \Phi''^2 - \varphi''^2, \dots (44)$$

where

$$\begin{aligned} \Phi'' &= \frac{1}{2} (v'_2 + v'_1) - v_{xk} = \Phi' + v_{Tk} - v_{xk} = \text{(to a first approximation)} \\ &= -\frac{1}{2m_{30}} \left[\frac{m_{01}}{RT_k} \left(\frac{m^2_{01}}{RT_k} + m_{11} \right) - \frac{2}{3} \frac{m^3_{01}}{R^2 T_k^2} - \frac{4m_{40}}{5m_{30}} \cdot \frac{m^2_{01}}{RT_k} \right] x + \\ &+ \frac{v_k(\alpha - \beta)}{\alpha T_k} (T - T_{xk}) + \frac{1}{2m_{30}} \left[m_{11} \left(\frac{m^2_{01}}{RT_k} + m_{11} \right) + \frac{2}{3} m_{21} - \right. \\ &\left. - \frac{4}{5} \frac{m_{11} m_{40}}{m_{30}} \right] \frac{T - T_{xk}}{\alpha T_k} \dots \dots \dots (45) \end{aligned}$$

and

$$\varphi''^2 = \frac{1}{4} (v'_2 - v'_1)^2 = \varphi'^2 = -\frac{m^2_{01}}{RT_k m_{30}} x + \frac{m_{11}}{m_{30}} \frac{T - T_{xk}}{\alpha T_k} \dots (46)$$

To this can be added

$$\Pi'' = \frac{1}{2} (p'_2 + p'_1) - p_{xk} = k_{01} (T - T_{xk}) \dots (47)$$

and

$$\pi'' = - \frac{m_{11}}{\alpha T_k} (T - T_{xk}) \varphi'' \dots (48)$$

To the first approximation equation (44) represents a parabola, of which the apex determines the elements of the critical point of contact for the mixture *x*. For we know that in the case of the critical point of contact $v'_2 = v'_1 = v_{x1}$, so that $\varphi'' = 0$ and $\Phi'' = v_{x1} - v_{xk}$. Hence it follows that¹⁾:

$$T_{x1} = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \dots (49)$$

$$p_{x1} = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \dots (50)$$

$$v_{x1} = v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{1}{3} \frac{m_{01}^2}{m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \right] \frac{x}{RT_k m_{11}} \dots (51)$$

In order to derive from this the equation of the border curve in the *p, v, T*-diagram, we must express *T* in terms of *p* and *v* by means of equation (13).

Then we find:

$$0 = (v - v_{xk})^2 - 2 \Phi''' (v - v_{xk}) + \Phi'''' - \varphi'''' \dots (52)$$

where

$$\begin{aligned} \varphi'''' = & - \frac{1}{2m_{30}} \left[\frac{m_{01}}{RT_k} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) - \frac{2}{3} \frac{m_{01}^3}{R^2 T_k^2} - \frac{4}{5} \frac{m_{40} m_{01}^2}{m_{30} RT_k} \right] x + \\ & + \frac{v_k (\alpha - \beta)}{k_{01} \alpha T_k} (p - p_{xk}) + \frac{1}{2k_{01} m_{30}} \left[\frac{m_{11}}{m_{01}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) + \frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{11} m_{40}}{m_{30}} - \right. \\ & \left. - \frac{k_{11} m_{11}}{k_{01}} \right] \frac{p - p_{xk}}{\alpha T_k} \dots (53) \end{aligned}$$

and

$$\varphi'''' = - \frac{m_{01}^2}{RT_k m_{30}} x + \frac{m_{11}}{k_{01} m_{30}} \frac{p - p_{xk}}{\alpha T_k} \dots (54)$$

To a first approximation (52) is a parabola on which

$$\frac{d^2 p}{dv^2} = 2 \frac{k_{01} m_{30}}{m_{11}} \alpha T_k = - 2 \frac{k_{01} k_{30}}{k_{11}}$$

as in the case of the border curve of the pure substance.

The apex of the border curve is the point of the maximum co-existence

¹⁾ We obtain the same formulae if we replace in equation (26) x_{T_k} by its value (17), put $T = T_{x1}$ and $x_{T1} = x$, solve T_{x1} and substitute it in (39) and (40).

pressure¹⁾. Let p_{xm} , v_{xm} , T_{xm} , be its coordinates, then we find by putting $\varphi''' = 0$ and $\Phi''' = v_{xm} - v_{xk}$

$$p_{xm} = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \dots \dots \dots (55)$$

$$v_{xm} = v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{1}{3} \frac{m_{01}^2}{m_{30}} \left(m_{21} + \frac{m_{01} m_{11}}{RT_k} - \frac{3 k_{11} m_{11}}{2 k_{01}} \right) \right] \frac{x}{RT_k m_{11}} \quad (56)$$

$$T_{xm} = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \dots \dots \dots (57)$$

Hence to the first approximation $p_{xm} = p_{xr}$ and $T_{xm} = T_{xr}$, but

$$v_{xm} - v_{xr} = - \frac{1}{2} \frac{m_{01}^2 k_{11}}{RT_k k_{01} k_{30}} x ; \dots \dots \dots (58)$$

for real mixtures, that is to say $x > 0$, the latter expression is necessarily negative, so that the critical point of contact is always situated on the descending (right) branch of the border curve. We cannot call it the vapour branch, because here the apex of the border curve is not the plaitpoint as in the p, v, x -diagram. The critical point of contact is situated thus, because the critical isothermal touches the border curve at that point, and because on that isothermal and hence also at the critical point of contact $T_{xr} > T_{xk}$ (at least for real mixtures),

therefore $\frac{\partial p}{\partial v} < 0$ for the border curve. This corresponds to a diagram-

matical representation of a p, v, T -diagram for a mixture given by KUENEN²⁾ and also with the experimental diagram for the mixture: 0.95 carbon dioxide, 0.05 hydrogen which I have given in my thesis for the doctorate. In spite of the small value of x , terms of higher order appear to have such a great influence in the case of this mixture that the apex of the border curve lies far outside the area investigated, and the border curve at the critical point of contact is no longer concave towards the v -axis but convex.

The plaitpoint elements for the mixture of composition x are found by substituting T_{xpl} for T and x for x_{Tpl} in equation (26), by solving T_{xpl} and substituting that value in (27) and (28). Then we find

$$T_{xpl} = T_k \left[1 + \frac{m_{01}^2 + RT_k m_{11}}{RT_k m_{11}} \alpha x \right] = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \dots \dots (59)$$

$$p_{xpl} = p_k + \left[p_k \beta + \frac{k_{01} m_{01}^2}{R m_{11}} \alpha \right] x = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \dots \dots (60)$$

1) Comp. HARTMAN, *Journ. Phys. Chem.*, 5, 437, 1901. Communications Leiden Suppl. N^o 3 p. 14.

2) *Zeitschr. f. physik. Chem.*, XXIV, 672, 1897.

$$v_{xpl} = v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{m_{01}}{2m_{s0}} \left(\frac{2}{3} m_{01} m_{s1} - \frac{1}{3} \frac{m_{01}^2 m_{s1}}{RT_k} - m_{s1}^2 \right) \right] \frac{x}{RT_k m_{s1}}, \quad (61)$$

which formulae, after some reductions, can be put in the form in which KEESOM has given them (*Comm.*, n^o. 75). Also the following well known equation ¹⁾ results directly from equations (59) and (60)

$$p_{xpl} - p_{xk} = k_{01} (T_{xpl} - T_{xk}) \dots \dots \dots (62)$$

which also according to equations (49), (50), (55) and (57) holds for the coordinates of the critical point of contact and for the apex of the border curve.

From the coordinates of the plaitpoint of mixtures of carbon dioxide with a small proportion of hydrogen ²⁾ ($x = 0, 0,05$ and $0,1$) I derive the following formulae

$$\left. \begin{aligned} T_{xpl} &= T_k (1 - 0,30 x + x^2) \\ p_{xpl} &= p_k (1 + 4,4 x + 11 x^2) \\ v_{xpl} &= v_k (1 - 0,40 x - 8 x^2) \end{aligned} \right\} \dots \dots \dots (63)$$

In connection with the formulae (16) I obtain directly from these:

$$\frac{p_{xpl} - p_{xk}}{T_{xpl} - T_{xk}} = 1,66 (1 + 2x),$$

in good harmony with equation (62) ($k_{01} = 1,61$) ³⁾. Using the value $k = -513$ ⁴⁾, I moreover find that the formulae (59) and (60) applied to mixtures of carbon dioxide and hydrogen become:

$$T_{xpl} = T_k (1 + 0,03 x) \quad \text{and} \quad p_{xpl} = p_k (1 + 6,4 x); \quad \dots (63')$$

hence the agreement with the formulae (63) is decidedly bad, as has also been remarked by KEESOM (*loc. cit.*, p. 13). We cannot, however, draw any conclusions from this; it is improbable that the inaccuracy of the data should cause this great deviation; but from the fact that terms of higher order produce such a great influence in the mixture $x = 0,05$, we see that quadratic formulae are very unfit for this comparison ⁵⁾, the more so as it appears from

¹⁾ Comp. v. D. WAALS, *Versl. Kon. Akad.*, Nov. 1897. It also follows directly from the equation of state (13) in connection with (15), by expressing that the elements of the plaitpoint satisfy this equation and by neglecting terms of a higher order than the first.

²⁾ VERSCHAFFELT, Thesis for the doctorate, Leiden 1899.

³⁾ Comp. also KEESOM, *loc. cit.*, p. 14.

⁴⁾ Derived from $\frac{RT_k}{p_k v_k} \frac{\partial^2 \pi}{\partial \omega \partial \tau} = -32,2$ (KEESOM, p. 12).

⁵⁾ By introducing the values for $x = 0,2$ (comp. VERSCHAFFELT, *Arch. Néerl.*, (2), 5, 649 etc., 1900, *Comm.* n^o. 65, and KEESOM, *loc. cit.* p. 12) they certainly will not become better.

KESOM's calculations (p. 13) that tolerably small variations in the values of α and β greatly influence the values of $\frac{dT_{xpl}}{dx}$ and $\frac{dp_{xpl}}{dx}$.

Accurate observations for mixtures with still smaller compositions are therefore highly desirable. As the v_{xpl} , and also the coordinates of the critical plaitpoint, are known with less certainty than the T_{xpl} and p_{xpl} , a comparison of the theoretical and the experimental values for these quantities is practically useless.

Again from the preceding equations $p_{xpl} = p_{xr}$, $T_{xpl} = T_{xr}$ to a first approximation, and

$$v_{xpl} - v_{xr} = -\frac{1}{2} \frac{m_{01}}{RT_k m_{30}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) x \dots \dots (64)$$

Hence the plaitpoint may lie either to the right or to the left of the critical point of contact; for positive x we have

	$m_{01} > 0$	$m_{01} < 0$
$RT_k^2 k_{11} \alpha > m_{01}^2$	$v_{xpl} < v_{xr}$; r. c. I	$v_{xpl} > v_{xr}$; r. c. II
$RT_k^2 k_{11} \alpha < m_{01}^2$	$v_{xpl} > v_{xr}$; r. c. II	$v_{xpl} < v_{xr}$; r. c. I

If the plaitpoint lies to the left of the critical point of contact, it may still lie either to the right or to the left of the apex, that is to say either on the descending or on the ascending branch of the border curve. In fact, according to (58) and (64) it lies:

1. to the right of the critical point of contact when m_{01} and $\frac{m_{01}^2}{RT_k} + m_{11}$ have the same signs,

2. between the critical point of contact and the apex when $\frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > m_{01} > 0$ or $0 > m_{01} > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right)$, and

3. to the left of the apex when $m_{01} > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > 0$ or $0 > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > m_{01}$.

In the p, v, T -diagram the plaitpoint has no geometrical meaning.

The expression that the coordinates of the critical point of contact and the plaitpoint satisfy the equation (44) gives, to the second approximation:

$$T_{xpl} - T_{xr} = -\frac{1}{4} \frac{m_{01}^2}{RT_k k_{30} k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right)^2 x^2 \dots \dots (65)$$

The right side is necessarily negative and therefore we always have $T_{xr} > T_{xpl}$, which also necessarily follows from the meaning of the critical point of contact. In the same way we find by means of equation (52) :

$$p_{xpl} - p_{xr} = \frac{1}{2} \frac{k_{01}}{k_{11}} \frac{m^2_{01}}{RT_k k_{s0}} \left(\frac{m^2_{01}}{RT_k} + m_{11} \right) \left[\frac{m_{01} k_{11}}{k_{01}} - \frac{1}{2} \left(\frac{m^2_{01}}{RT_k} + m_{11} \right) \right] x^2. \quad (66)$$

12. The condensation.

The line which indicates the relation between the pressure and the volume during the condensation, the so-called experimental isothermal, extends between the two points p'_1, v'_1 and p'_2, v'_2 (the points where the condensation begins and ends) but we can also imagine it to extend beyond those two points, although there it has only a mathematical meaning; for beyond those two points the quantity of one of the phases would be negative. In order to find the equation of the experimental isothermal we must seek at each volume for the pressure at which the two phases into which the mixture splits, can co-exist. For this purpose I return to the projection on the x, v -plane (§ 8) of the ψ -surface belonging to the temperature T . If v_1, x_1 and v_2, x_2 are the phases into which the mixture x splits when the volume v is reached ($v_2 > v > v_1$), the point v, x lies on the straight line connecting the points v_1, x_1 and v_2, x_2 and hence we have this relation :

$$\frac{v - vTk - \Phi}{x - xTk - \Xi} = \frac{\varphi}{\xi}, \quad \dots \dots \dots (67)$$

where Φ, Ξ, φ and ξ have the same meaning as in § 5. If p_1 is the pressure at which the two phases x_1 and x_2 co-exist then we obtain the equation of the experimental isothermal by expressing the quantities Φ, Ξ, φ and ξ of equation (67) in p_1 by means of the equations (22), (23), (24) and (25).

That this experimental isothermal passes through the two points v'_1, x and v'_2, x follows directly from the way in which its equation has been derived; we also obtain it from the substitution of v'_1, x'_1 — or v'_2, x'_2 — for v, x , which involves the substitution of v'_1, x'_1 for v_1, x_1 — or of v'_2, x'_2 for v_2, x_2 .

By successive approximations (67) is brought to the form :

$$p_1 = pTk + m_{01} (x - xTk) - \frac{m^2_{01}}{RT_k} (v - vTk) x + \dots; \quad \dots (68)$$

if we consider only the three first terms, this is the equation of a straight line, hence of that connecting the two phases where the condensation begins and ends. In connection with (18) we find, neglecting terms of higher order,

$$p - p_1 = m_{11} (v - v_{Tk}) (x - x_{Tk}) + \frac{m_{01}^2}{RT_k} (v - v_{Tk}) x + m_{00} (v - v_{Tk})^2,$$

and according to (33) this may be written

$$p - p_1 = k_{30} (v - v_{Tk}) [(v - v_{Tk})^2 - \varphi'^2].$$

We see that in this form the experimental isothermal intersects the theoretical at three points ¹⁾, viz. $v = v_{Tk} + \varphi'$, $v = v_{Tk} - \varphi'$ and $v = v_{Tk}$ (all to the first approximation); the two first points are the points at which condensation begins and ends (Φ' has been neglected as being of higher order than φ'), the third lies between the two first.

When $v_{Tk} + \varphi' > v > v_{Tk}$, that is to say at the beginning of the condensation, $p > p_1$ and the theoretical isothermal lies above the experimental; when $v_{Tk} > v > v_{Tk} - \varphi'$, i.e. at the end of the condensation, $p > p_1$ and the experimental isothermal is the higher ²⁾; this, indeed, follows necessarily from the *s*-shape of the theoretical isothermal, and the approximate straightness of the experimental.

According to thermodynamics the two areas enclosed by the theoretical and the experimental isothermal must be equivalent ³⁾, that is to say :

$$\int_{v_1}^{v_2} (p - p_1) dv = 0.$$

or

$$\int_{-\varphi'}^{+\varphi'} (p - p_1) d(v - v_{Tk}) = 0,$$

and this actually follows from the form, found just now for $p - p_1$.

This has only been proved for the terms considered here; but obviously it must also be possible to prove this for terms of higher order.

13. The *p*, *T* diagram.

a. The vapour pressure curve of the pure substance. We have found to a first approximation :

$$p_1 = p_k + k_{01} (T - T_k).$$

As k_{01} is positive, this straight line rises and terminates at the

¹⁾ Comp. for this HARTMAN, Comm., n^o. 56 and Suppl. n^o. 3 p. 25; Journ. Phys. Chem., 5, 450, 1901.

²⁾ Here the proof is only given for mixtures with small composition. For a general proof comp. KUENEN, Zeitschr. f. Physik. Chem., XLI, 46, 1902.

³⁾ It has escaped BLUMCKE's notice, who mentions this theorem in 1890 (Zeitschr. f. physik. Chem., VI, p. 157) that it occurs already in a treatise of VAN DER WAALS of 1880 (Verh. Kon. Akad., Bd. 20, p. 23).

point p_k , T_k . T_k is a maximum temperature, so that this curve lies in the third quadrant ($S'O$, fig. 16.)

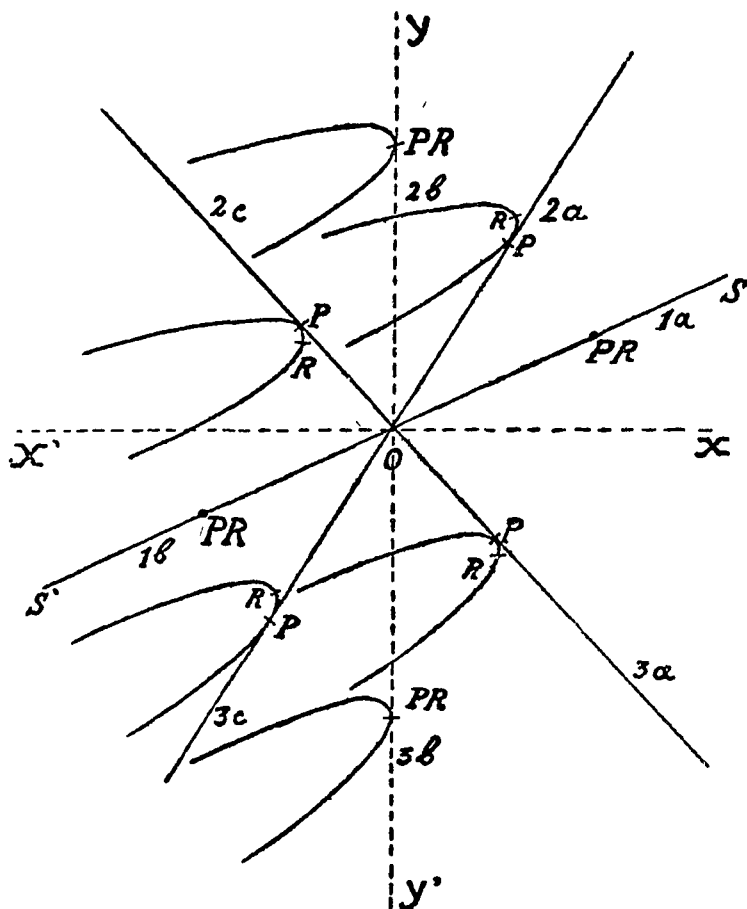


Fig. 16.

b. *The plaitpoint curve.* According to equation (27)

$$p_{T,p} = p_k + \left[p_k \beta - \frac{m_{01}^2}{m_{01}^2 + RT_k m_{11}} \right] \frac{T - T_k}{\alpha T_k} = p_k + \left(k_{01} - \frac{RT_k k_{11} m_{01}}{m_{01}^2 + RT_k m_{11}} \right) (T - T_k)$$

This curve may have all possible directions. If we consider only real mixtures ($x > 0$), it extends only on one side of the point p_k , T_k , namely that corresponding to such values that $T - T_k$ and $m_{01}^2 + RT_k m_{11}$ have the same signs (according to equation 26').

With regard to the position of the plaitpoint curve we distinguish the following cases :

1. $m_{01} = 0$. $p_{T,p} = p_k + k_{01} (T - T_k)$, hence the beginning of the plaitpoint curve will lie either in the direction of the vapour pressure

curve of the pure substance or will co-incide with it as $T > T_k$ or $T < T_k$, that is to say, according to (26'), as α is positive or negative. In the first case (1a), therefore, the plaitpoint curve will lie in the first quadrant (OS fig. 16), in the second case (1b) in the third quadrant (OS'). We have noted that then the plaitpoint elements of a mixture co-incide with the critical elements which the mixture would have, if it remained homogeneous, hence the mixture behaves like a pure substance. This is the case $\frac{\partial^2 \psi}{\partial x \partial v} = 0$ already discussed by VAN DER

WAAALS¹⁾; in this case there is a mixture — here it must be the pure substance itself — for which the vapour tension is a maximum or a minimum, and indeed it follows from the expression for $p_1 - p_k$ in this case²⁾ that $\left(\frac{\partial p_1}{\partial x_1}\right)_{x_1=0} = 0$.

2a. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} > 0$. $\frac{dp_{T_{pl}}}{dT} > k_{01}$, so that the plaitpoint curve lies in the angle SOY because $T - T_k$ must be also positive.

2b. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} = 0$, $\frac{dp_{T_{pl}}}{dT} = \pm \infty$, and the beginning of the plaitpoint curve co-incides with OY^3).

Thus we have here the second special case of the shape of the plaitpoint curve investigated by VAN DER WAAALS, i e. where there is a maximum or minimum temperature, here the critical temperature of the pure substance. Really in this case (§ 10,2), as $p_{T_k} - p_k$ is of higher order than $p_{T_{pl}} - p_k$,

$$T - T_k = \frac{Kk_{30}}{k_{11}} (p_{T_{pl}} - p_k)^2$$

hence $\left(\frac{dT_{pl}}{dp_{T_{pl}}}\right)_k = 0$. $T > T_k$, that is to say T_k is the minimum plaitpoint temperature, when $K > 0$, this is the case where the border curve and the connodal line are hyperbolae (mixtures of HARTMAN'S third type). And $T < T_k$, that is so say T_k is a maximum, when $K < 0$; in this case the border curve and the connodal line are ellipses (mixtures of the second type).

2c. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} < 0$. $\frac{dp_{T_{pl}}}{dT} < k_{01}$, and because

¹⁾ Arch. Néerl., (1), 30, 266, 1896.

²⁾ Comp. preceding communication, p. 267; to the first approximation $\Xi = x_1$.

³⁾ Not with OY' , for, as in this case $p_{T_k} - p_k$ and x_{T_k} are infinitely small with respect to $p_{T_{pl}} - p_k$ and $x_{T_{pl}}$ (§ 10,2), according to (29) $p_{T_{pl}} - p_k = m_{01} x$, so that for $x > 0$, $p_{T_{pl}} > p_k$.

$T - T_k$ must also be negative the plaitpoint curve lies in the angle $S'OY$.

3a. $m_{01} < 0$ and $m^2_{01} + RT'_k m_{11} > 0$, $\frac{dp_{rpl}}{dT} < k_{01}$, but $T - T_k > 0$, and hence in the angle SOY' .

3b. $m_{01} < 0$ and $m^2_{01} + RT_k m_{11} = 0$. The plaitpoint curve touches OY' ¹⁾. Compare moreover 2b.

3c. $m_{01} < 0$ and $m^2_{01} + RT_k m_{11} < 0$. $\frac{dp_{rpl}}{dT} > k_{01}$, but $T - T_k > 0$, hence in the angle $S'OY'$.

From this it appears that $\frac{dp_{rpl}}{dT}$ can take all possible values. According to VAN DER WAAALS²⁾, however, this is not true and the case $\frac{dp_{rpl}}{dT} = \frac{pk}{T_k}$ for instance could never occur. But it should be borne in mind that this rule of VAN DER WAAALS does not rest on an exclusively thermodynamic reasoning, but also on special suppositions about the form of the equation of state, which naturally corresponds to special relations between the co-efficients introduced here, and as a matter of course it is always possible that the numerical values of the coefficients are such, that one or more of the cases considered are excluded.

c. *The critical point of contact curve.* To the first approximation $p_T = p_{Tpl}$, so that the critical point of contact curve to a first approximation co-incides with the plaitpoint curve and the considerations in *b* hold also for this line. Equation (43) shows moreover that to a second approximation.

$$p_T - p_{Tpl} = -\frac{1}{4} \frac{m^3_{01} k^2_{11}}{RT_k m_{30} (m^2_{01} + RT_k m_{11})} (T - T_k)^2,$$

from which it follows that the critical point of contact curve lies above the plaitpoint curve when m_{01} and $m^2_{01} + RT_k m_{11}$ have the same signs; this occurs in the cases 2a and 3c just mentioned, hence in the angles SOY and $S'OY'$. In the other cases the point of contact curve is the lower. Moreover the two curves also co-incide to a second approximation if $m_{01} = 0$ and even if $m^2_{01} + RT_k m_{11} = 0$. $\left(\frac{dp_{Tpl}}{dT} = \frac{dp_T}{dT} = \pm \infty\right)$ although in that case $p_T - p_{Tpl}$ is not zero to the second approximation.

d. *The border curves.* This position of the critical point of con-

¹⁾ $p_{rpl} < p_k$ for $x > 0$; comp. preceding note.

²⁾ Arch. Néerl., (2), 2, 79, 1898.

fact curve with respect to the plaitpoint curve corresponds to the position of the critical point of contact with respect to the plaitpoint on the border curves, represented in an exaggerated way in fig. 16. To the second approximation those border curves are parabolæ which touch the plaitpoint curve and have a vertical tangent at the critical point of contact, but to the first approximation they co-incide with the axis which is conjugate to the vertical chords and the equation of which according to (47), is :

$$p = p_{\lambda k} + k_{01} (T - T_{xk}) = p_{xpl} + k_{01} (T - T_{xpl}).$$

Hence these straight lines are parallel with the vapour pressure curve of the pure substance and terminate, on the plaitpoint curve, in the plaitpoint of the mixture to which they belong.

14. Continuation of § 9: the critical point of contact.

Mr. KESOM kindly informs me that the method given by him in Comm. N^o. 75 and which leads very easily to the constants of the plaitpoint presents difficulties when applied to determine the constants of the critical point of contact.

He however succeeded, by means of the method used by me in § 9, in deriving the constants of the critical point of contact from the formulae ¹⁾, given by KORTEWEG in his paper "Ueber Faltenpunkte", Wien. Sitz. Ber. Bd. 98, p. 1154, 1889, and proceeded thus.

It has been shown in Comm. N^o. 59^b, p. 36 ²⁾ that instead of deducing the coexistence-conditions by rolling the tangent-plane over the ψ -surface, we can also obtain them by rolling the tangent-plane over a ψ' -surface, the latter being deduced from the ψ -surface by making the distance, measured in the direction of the ψ -axis, between this surface and a fixed tangent-plane the third coordinate perpendicular to x and v . We can go a step further in this direction by deducing a ψ'' -surface by means of KORTEWEG's projective transformation ³⁾

$$\psi'' = \psi' - v' \left(\frac{\partial \psi'}{\partial v'} \right)_{pl} - x' \left(\frac{\partial \psi'}{\partial x'} \right)_{\nu l}$$

$$x'' = x' - m v'$$

$$v'' = v'$$

Here

$$\psi' = \psi - \psi T_{pl}$$

$$x' = x - x T_{pl}$$

$$v' = v - v T_{pl}$$

¹⁾ The simplest way of proving that the case $c_1 = \infty$ in KORTEWEG's formula (4) does not influence the present deduction, is by noting that the area over which the development is applied is infinitely small in comparison with $x T_{pl}$.

²⁾ Proceedings Sept. 1900, p. 296.

³⁾ See KORTEWEG l. c. equation 38.

As

$$\left(\frac{\partial \psi''}{\partial x''}\right)_1 = \left(\frac{\partial \psi''}{\partial x''}\right)_2$$

$$\left(\frac{\partial \psi''}{\partial v''}\right)_1 = \left(\frac{\partial \psi''}{\partial v''}\right)_2$$

$$\psi_1'' - x_1'' \left(\frac{\partial \psi''}{\partial x''}\right)_1 - v_1'' \left(\frac{\partial \psi''}{\partial v''}\right)_1 = \psi_2'' - x_2'' \left(\frac{\partial \psi''}{\partial x''}\right)_2 - v_2'' \left(\frac{\partial \psi''}{\partial v''}\right)_2$$

when

$$\left(\frac{\partial \psi'}{\partial x'}\right)_1 = \left(\frac{\partial \psi'}{\partial x'}\right)_2, \text{ etc.}$$

it is also possible to obtain the coexisting phases by rolling a tangent-plane over this ψ'' -surface. ψ'' as function of x' and v'' presents the form

$$\psi' = c_1 x''^2 + d_3 x'' v''^2 + e_5 v''^4 \quad (\text{KORTEWEG'S equation 4}).$$

Hence for the connodal curve KORTEWEG'S deduction may be applied, and we find for the equation of that curve

$$x'' = -2 \frac{e_5}{d_3} v''^2 \quad (\text{equation 8 l. c}).$$

m is now found from

$$m \left(\frac{\partial^2 \psi}{\partial x^2}\right)_{vT} + \left(\frac{\partial^2 \psi}{\partial x \partial v}\right)_T = 0 \quad (\text{equation 34}),$$

where the differential quotients are taken for the plaitpoint, so that for a substance with a small proportion of one component, to the first approximation

$$m = \frac{1}{MRT_k} \left(\frac{\partial p}{\partial x}\right)_{vT} {}^{xT} p_l.$$

Further we may put, leaving out terms of higher order, according to equation (39)

$$d_3 = -\frac{1}{2MRT_k} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\}$$

$$e_5 = -\frac{1}{24} \left(\frac{\partial^3 p}{\partial v^3}\right)_{xT}.$$

Using the property that for the point of contact $\frac{dx}{dv} = 0$, this yields:

$$v_{T'} - v_{T'pl} = 3 \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}}{(MRT_k)^2 \left(\frac{\partial^3 p}{\partial v^3}\right)_{xT}} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\} {}^{xT} p_l$$

and

$$x_{Tr} - x_{T_{pl}} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}^2}{(MRT_k)^2 \cdot \frac{\partial^3 p}{\partial v^3}} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right) \right\} x^2 T_{pl}.$$

So that for $x=0$: $\frac{dx_{Tr}}{dT} = \frac{dx_{T_{pl}}}{dT}$, or $\frac{dT_{Tr}}{dx} = \frac{dT_{pl}}{dx}$, from which we easily derive that also $\frac{dp_{Tr}}{dx} = \frac{dp_{pl}}{dx}$ so that in the pT -diagram the point of contact curve and the plaitpoint curve touch at the ends. We find further that with the same x :

$$T_{Tr} - T_{xpl} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}^2}{(MRT_k)^4 \cdot \left(\frac{\partial^3 p}{\partial v^3}\right) \left(\frac{\partial^2 p}{\partial v \partial T}\right)} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\} x^2.$$

from which $p_{Tr} - p_{xpl}$ can be easily found.

If, as in Communication N^o. 75 (Proceedings Nov. 1901), we introduce the law of corresponding states, we find:

$$v_{Tr} - v_{T_{pl}} = 3 C_4 v_k \frac{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)}{C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4 \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right] x$$

$$T_{Tr} - T_{xpl} = \frac{3}{2} \frac{\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2}{C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right) \cdot C_4 \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4 \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right] x^2.$$

Physiology. — "On the structure of the light-perceiving cells in the spinal cord, on the neurofibrillae in the ganglioncells and on the innervation of the striped muscles in amphioxus lanceolatus."

By Dr. J. BOEKKE. (Communicated by Prof. T. PLACE).

In connection with a former note¹⁾ I mean to describe here some points of the histology of the central and peripheral nervous system of amphioxus lanceolatus, especially to follow the neurofibrillae in their arrangement and distribution in the cells and in the muscle-plates.

This paper is the outcome of observations begun in 1900 in the Stazione Zoologica at Naples, but then not carried any farther, to study the structure of the pigmented cells of the spinal cord. During

¹⁾ Proceedings of the Royal Academy of Amsterdam. Meeting of April 19, 1902.