

Citation:

Verschaffelt, J.E., Contribution to the knowledge of Van der Waals' psi-surface. VIII. The psi-surface in the neighbourhood of a binary mixture which behaves as a pure substance, in:
KNAW, Proceedings, 6, 1903-1904, Amsterdam, 1904, pp. 649-658

Physics. — “Contributions to the knowledge of VAN DER WAALS’ ψ -surface. VIII. The ψ -surface in the neighbourhood of a binary mixture which behaves as a pure substance.” By Dr. J. E. VERSCHAFFELT. Supplement n°. 7 to the Communications from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903).

General part.

Distillation of a mixture without its composition being altered, and reversely also condensation of a mixture by decrease of volume, without variation of pressure, quite as a pure substance, can only occur at one special temperature. Experiments of KUENEN¹⁾ have shown for the first time that this phenomenon may be observed in the neighbourhood of the plaitpoint of the mixture; this circumstance has been theoretically investigated and explained by VAN DER WAALS²⁾.

If a mixture behaves as a pure substance just at the plaitpoint temperature the critical point of the homogeneous mixture, the critical point of contact and the plaitpoint coincide at a same point which may therefore properly be called the critical point of the special mixture and of which I shall represent the elements, as for a simple substance, by T_k , p_k and v_k .

Then according to VAN DER WAALS³⁾ we have at the plaitpoint $\left(\frac{\partial p}{\partial x}\right)_{v_k} = 0$. Hence the isothermals of two neighbouring mixtures at the same temperature must intersect in pairs, so that the system of isothermals of the mixtures at the critical temperature of the special mixture must agree with fig. 16 of my paper in these Proc. Oct. 25 1902 p. 345. In the annexed figure a similar system of isothermals is drawn according to observations of QUINT⁴⁾ with mixtures of hydrochloric acid and ethane.

Although the special mixture behaves as a simple substance at the critical point, yet it does not follow from this that its border curve on the p, v, t diagram may be found in the same way as for a simple substance, i. e. by making use of the theorem of MAXWELL-CLAUSIUS. For just below the critical temperature the pressure no longer remains unchanged during the condensation and the experimental isothermal is no longer perfectly parallel with the v -axis,

¹⁾ Phil. Mag., 40, 173—194, 1895. *Comm. phys. lab. Leiden*, n°. 16.

²⁾ *Arch. Néerl.*, 30, 266, 1896.

³⁾ *Contin.* II p. 116.

⁴⁾ Thesis for the doctorate, Amsterdam 1900.

though the variation of pressure is vanishingly small. Consequently the system of isothermals satisfies the law of corresponding states, but the border curve does not necessarily do so. Hence we shall see that for the border curve this is only the case to a first and a second approximation.

The ψ -surface. I shall represent by x_k the composition of the mixture which behaves as a simple substance. In the neighbourhood of the critical point the system of isothermals of this mixture may be represented by the equations (2) and (2') of my paper in these proc. Oct. 25 1902 p. 321; for the rest all the considerations of sections 2 and 3 of the same paper are directly applicable, except that $x-x_k$ must everywhere be substituted for x , and hence also $x_{Tk}-x_k$ for x_{Tk} . Thus we find back, for the system of isothermals of the mixtures at a temperature which differs little from T_k , the equations (18) and (18'), where $x-x_{Tk}$ is vanishingly small, but not x and x_{Tk} separately; from the circumstance that at the critical point $\left(\frac{\partial p}{\partial v}\right)_v = 0$, it also follows that $m_{01} = 0$; and because $m_{01} = p_k \beta - k_{01} T_k \alpha$ we must have:

$$\frac{\beta}{\alpha} = k_{01} \frac{T_k}{p_k} = \left(\frac{\partial p}{\partial v}\right)_k = 7,3 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Finally we may remark that whereas in fig. 16 (l. c.) the dotted line which, agreeing with $x < 0$, had no physical meaning, this line can really exist here, since $x < x_k$ may as well be imagined as $x > x_k$.

The equation of the ψ -surface may now be written in this case:

$$\begin{aligned} \psi = & -m_0 (v-v_{Tk}) - \frac{1}{2} m_1 (v-v_{Tk})^2 - \frac{1}{3} m_2 (v-v_{Tk})^3 - \frac{1}{4} m_3 (v-v_{Tk})^4 \dots \\ & + RT x_k (1-x_k) \left[\frac{1}{1.2} \frac{(x-x_k)^2}{x_k^2 (1-x_k)^2} + \frac{2x_k-1}{2.3} \frac{(x-x_k)^3}{x_k^3 (1-x_k)^3} + \right. \\ & \left. + \frac{3x_k^2-3x_k+1}{3.4} \frac{(x-x_k)^4}{x_k^4 (1-x_k)^4} + \dots \right], \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

where again a linear function of x is omitted, while $m_{00} = p_{Tk}$, and further m_{01} , m_{10} and m_{20} may be put equal to zero.

The border curve at a temperature T . In the same way as before¹⁾ I find, putting

$$\begin{aligned} \frac{1}{2} (v_2 + v_1) - v_{Tk} &= \Phi, & \frac{1}{2} (v_2 - v_1) &= \varphi \\ \frac{1}{2} (x_2 + x_1) - x_{Tk} &= \Xi, & \frac{1}{2} (x_2 - x_1) &= \xi, \end{aligned}$$

v_1, v_2, x_1, x_2 representing the molecular volumes and the molecular compositions of the coexisting phases, that

¹⁾ These Proc. V, Oct. 25 1902, p. 330.

$$\varphi^2 = -\frac{m_{11}}{m_{30}} \mathbb{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

border curve of the mixture x in the p, v, T diagram. To the first approximation its equation is:

$$p - p_{xk} = - \frac{k_{01} k_{30}}{k_{11}} (v - v_{xk})^2, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

as for a simple substance¹⁾. Hence to the first approximation the border curve satisfies the law of corresponding states.

That the border curve, apart from the deviations existing already in pure substances does not altogether satisfy the law of corresponding states, has a double cause. It is not only for mixtures which differ little from the special mixture x_k that the experimental isothermal shows a slight slope, but this is even the case for the mixture x_k itself; only at the plaitpoint temperature it is perfectly horizontal so that already for the mixture x_k the border curve must deviate from the law of corresponding states. If as before¹⁾ we develop the equation of the experimental isothermal:

$$\frac{v - v_{Tk} - \Phi}{x - x_{Tk} - \Xi} = \frac{\varphi}{\xi},$$

we find:

$$p - p_{Tk} = \left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right) (x - x_{Tk})^2 - \\ - 8m_{30}^2 \frac{\left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right)^2}{m_{11}^2 + \frac{2RT m_{30}}{x_k(1-x_k)}} (v - v_{Tk}) (x - x_{Tk})^2 + \dots (12)$$

and hence, for $x = x_k$,

$$p = p_k + k_{01} (T - T_k) - 8m_{30}^2 \frac{\left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right)^2}{m_{11}^2 + \frac{2RT m_{30}}{x_k(1-x_k)}} (v - v_k) \frac{(T - T_k)^2}{\alpha^2 T_k^2} + \dots (13)$$

only for $x_k = 0$ or 1 , that is to say for the pure substances, the third term is left out — and in the same way all the terms which contain $v - v_k$.

If now by elimination of $T - T_k$ between the equation of state of the mixture x_k (equation (2), l. c. p. 323) and the experimental isothermal (10), we search for the border curve for that special mixture, we see that the slope of the experimental isothermal only influences the third term — viz. with $(v - v_k)^4$ — in the development (11) of the border curve, so that this border curve only to a third approximation shows a deviation from the law of corresponding

¹⁾ These Proc. V, Oct. 25, 1902, p. 336.

states. Also for a neighbouring mixture this deviation is only perceptible in third approximation, while for mixtures with a small composition, i. e. on the edge of the ψ -surface, it exists already in second approximation.

The cause of this smaller deviation in mixtures near the special mixture must be looked for in the circumstance that those mixtures in all their qualities deviate only in second approximation from a single substance; thus we deduce from equation (11) that the critical points: plaitpoint, critical point of contact, critical point of the homogeneous mixture and point of maximum coexistence pressure, differ only in second approximation, so that the four curves (in the space with p , v and T as coordinates), which connect these critical points of all mixtures touch each other at the critical point of the special mixture, which in general is not the case at the two critical points of the pure components.

Application to mixtures of hydrochloric acid and ethane.

The experiments of KUENEN with mixtures of ethane and nitrous oxide, the first where the existence was shown of a mixture that in its critical phenomena agrees with a simple substance, does not allow us to form a complete image of the conduct of neighbouring mixtures. Besides, his investigations were only aimed at the discovery of the second kind of retrograde condensation, and the existence of that special mixture was a new discovery, and not the object of the investigation. Suitable data for our purpose are given by the measurements of QUINT on mixtures of hydrochloric acid and ethane; according to QUINT the composition of the mixture which behaves as a simple substance is $x_k = 0.44$, i. e. 0.44 gram molecules ethane and 0.56 gram molecules hydrogen chloride. Mixtures behaving as a pure substance have also been observed by CAUBET¹⁾ in his experiments with CH_3Cl and SO_2 ; as CAUBET however investigated only two mixtures of this binary system, his data are insufficient for our purpose.

In order to proceed with the mixtures investigated by QUINT in the way indicated by KAMERLINGH ONNES, we must determine in the first place the critical elements of the homogeneous mixture T_{xk} , p_{xk} , v_{xk} .

Instead, however of drawing, the $\log pv$, $\log v$ or $\frac{pv}{T}$, $\log p$ diagrams it was sufficient, as in the case of my former investigations²⁾ of the

¹⁾ Liquéfaction des mélanges gazeux, Paris, 1900.

²⁾ Arch. Néerl., (2), 5, 644, 1900.

mixtures of carbon dioxide and hydrogen to use the $\log p$, $\log v$ diagrams, as I found that not only the logarithmical diagrams of the pure substances but also those of the four mixtures investigated could be made to coincide with the logarithmical diagram of carbon dioxide by shifting them parallel to each other.

Unfortunately QUINT made only few observations in the neighbourhood of the critical point, a circumstance which rendered this investigation rather difficult. For it is by means of those very parts situated in the neighbourhood of the point of inflection that the superimposing of the diagrams may be obtained in the most accurate way, while in the area of the larger volumes a shifting within rather wide limits does not cause a perceptible deviation of the superimposed diagrams. Especially the want of observations in the neighbourhood of the critical point in the case of hydrochloric acid is to be regretted because the difference between the critical point given by QUINT and that found by shifting is much larger than we should expect, the diagrams covering each other in a satisfactory way. The more so because, when for ethane and carbon dioxide the diagrams are made covering each other in the observed area the critical points too coincide.

Here follow the values found, for the different mixtures, as elements of the critical point of the homogeneous mixture:

x = (pure HCl)	0,1318	0,4035	0,6167	0,7141	(1 pure C_2H_6)	
x_k =	42°,5	30°,0	26°,4	25°,8		
p_{xk} =	77,3 atm.	65,5	58,6	55,7		
v_{xk} =	0,00429	0,00190	0,00543	0,00570		
t_{xpl} =	51°,3	43°,1	30°,53	27°,25	27°,37	31°,88
p_{xpl} =	84,13 atm.	77,51	65,42	54,30	56,84	48,94
v_{xpl} =	0,00380	0,00420	0,00471	0,00540	5,00576	0,00652
C_4 =	3,48	3,46	3,45	0,45	3,50	

In order to make a comparison I have written in this table the plaitpoint elements of the mixtures as observed by QUINT, and in the last line the values of the expression $C_4 = \frac{RT_{xk}}{p_{xk} v_{xk}}$ which here are about the same for all the mixtures, especially in the neighbourhood of the special mixture. By means of QUINT's data we find however, for HCl, the much larger number $C_4 = 3,71$; this deviation evidently must be brought in connection with the other one I mentioned before.

If we draw the t_{xk} and t_{xpl} as ordinates and x as abscis we obtain two curves which obviously touch each other at one point; it is difficult, however, to define this point of contact precisely. If the same is done with p_{xk} and p_{xpl} , the determination of the point of contact of the two curves is even less certain, owing to the circumstance that, according to the table above, for $x = 0,4035 = p_{xk} > p_{xpl}$, which surely follows from the inaccuracy of the method. And the deduction of this point of contact from a graphical representation of the v_{xk} and v_{xpl} is quite impossible because these volumes are known by no means with sufficient accuracy.

Therefore it seems to me that the best method is that of QUINT who deduced the composition of the special mixture from the shape of the plaitpoint curve by searching on this curve the point where the bordercurve, which terminates at that point, touches the plaitpoint curve. That point may be determined fairly accurately: we find for its coordinates $t_k = 29^\circ,0$ and $v_k = 63,8$ atms., whence again $x_k = 0,44$ and $v_k = 0,00500$.

By means of the graphical representations of the t_{xk} , p_{xk} and v_{xk} I find in the neighbourhood of $x_k = 0,44$, $\frac{dT_{xk}}{dx} = -20$, $\frac{dp_{xk}}{dx} = -30$ and $\frac{dv_{xk}}{dx} = 0,0020$; hence $\alpha = -0,07$ $\beta = -0,50$ and $\gamma = 0,40$, so that the relations $\gamma = \alpha - \beta$ in $\frac{\beta}{\alpha} = 7,3$ are confirmed in a satisfactory way.

By means of QUINT's observations, by inter- or extrapolation, partly also by using the law of corresponding states and the values of t_{xk} , p_{xk} , v_{xk} found above, I have drawn the isothermals for the 6 x -values considered, at the critical temperature $29^\circ,0$ C. of the special mixture $x = 0,44$. Those isothermals are represented in the annexed figure, which thus shows the p - v -diagram of the mixtures at the temperature $29^\circ,0$ C. The dot-dash line is the critical $x = 0,44$ with the critical point in C . The isothermal $x = 0,40$ is a dash line in the unstable part; owing to their small curvature the experimental isothermals are represented by straight lines. The border curve is a complete line like the observable parts of the isothermals.

Under the p , v -diagram I have represented the projection on the v , x -surface. The critical isobar (63.8 atms.) is represented by a dot-dash line; some other isobars are drawn, like the projection of the connodal line (also projection of the afore-mentioned border curve), while the isobars in the unstable part, i. e. within the projection, are dotted. The temperature 29° being lower than the critical temperature

of pure ethane ($31^{\circ}.88$), the connodal line consists of another part, which I have not drawn, however, in order not to make the figure uselessly intricate. This second piece should have its apex, the critical point of contact, at about $x_{Tk} = 0.92$, and $v_{Tk} = 0.0063$, and would intersect the axis $x = 1$ at $v = 0.00472$ and $v = 0.01031$.

To this second piece of the connodal a second border curve corresponds which would begin at a height $p = 46.1$ (maximum tension of ethane at $29^{\circ}.0$ C.) and terminate at the plaitpoint $p_{Tpl} = 51.2$, $v_{Tpl} = 0.0063$. But this border curve too I have omitted like the isothermal of pure ethane.

At the lower part of the figure it may be seen that the isobars in the neighbourhood of the critical point C , indeed to the first approximation, are hyperbolae of which one of the asymptotes, which agree with the critical pressure, is parallel to the v -axis, the other cuts this axis at a given angle. To the second approximation the first asymptote is a parabola which coincides with the projection of the connodal line.

It were useless to investigate whether indeed the border curve is of the fourth degree and the connodal of the second degree; for this the data are not numerous enough and the drawing not sufficiently accurate. But it is obvious why the border curve should be of a higher order than the connodal. The p, v, x -surface, of which the projections on the surfaces p, v and x, v are shown in the fig., is in the neighbourhood of the critical point a saddle-shaped surface, which at the upper part of the figure is seen parallel to the tangent surface at the point C . The isothermals of the mixtures $x = 0$, $x = 0.14$ and $x = 0.40$ are situated on the slope turned towards us; the latter over a fairly extensive range (of large volumes to about $x = 0.006$) forms nearly the border of the surface; the critical isothermal lies just beyond that border, but becomes visible at C and remains visible for small volumes. The isothermals $x = 0.62$, $x = 0.71$ and $x = 1$ occur on the back of the p, v, x -surface, yet for small volumes they become visible. The parabola:

$$p - p_{Tk} = - \frac{1}{4} \frac{m_{11}^2}{m_{02}} (v - v_{Tk})^2,$$

which envelops the isothermals in the neighbourhood of the point C (l. c. p. 344 and fig. 16) is the apparent outline of the surface in that neighbourhood.

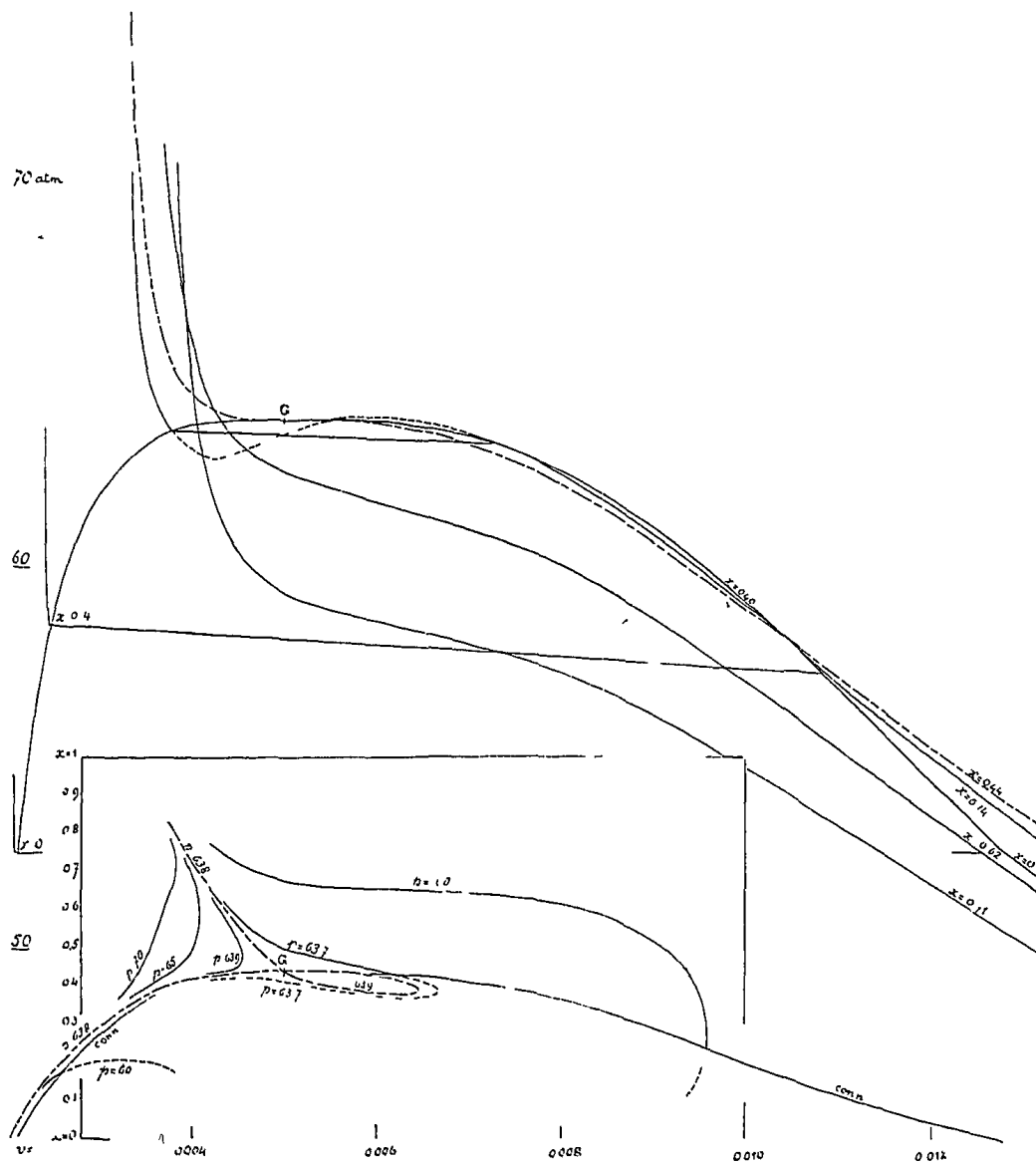
The lower part of the figure represent the surface seen from above; the isobars are there level-curves. The critical isobar forms a loop which agrees with the described shape of the surface. A section of a horizontal surface situated a little higher consists of two pieces,

of which one, lying within the loop is closed. Within the loop therefore, the surface shows an elevation of which the top almost agrees with $x = 0.40$, $v = 0.06$, $p = 63.9$. For higher horizontal surfaces the section consists of one branch only. For horizontal surfaces corresponding to $p < 63.8$ atm., the sections also consist in one branch which surrounds the critical loop.

From $x = 0$ the bordercurve occurs on the front of the p, v, x -surface, but reaches the border almost at the volume 0.008, then occurs on the back where it remains until the point C , and returns to the front. At the point C the osculation plane to the border curve, at the same time the tangent plane to the surface, is horizontal; the projection on the x, v -plane shows the border curve more and more in its true shape the more we approach the point C ; whereas in the upper projection that border curve is seen more and more in an oblique direction and finally in a tangent one, so that it must appear flattened, which accounts for the higher order of the border curve in that projection.

(March 23, 1904).

J E VERSCHAFFELT 'Contributions to the knowledge of van der Waals' \downarrow surface VIII The \downarrow surface in the neighbourhood of a binary mixture which behaves as a pure substance"



Proceedings Royal Acad Amsterdam Vol VI