

Citation:

Johannes Diderik van der Waals, Contribution to the theory of binary mixtures. XIII, in: KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 698-715

$$(\omega\omega) = \frac{\mu_1}{a_2} \left\{ 4 A \varepsilon_1 \cos \alpha - B \varepsilon_2 \cos (\alpha + \beta) \right\},$$

$$(\omega'\omega') = \frac{\mu_3}{a_3} \left\{ 4 A \varepsilon_2 \cos \alpha' - B \varepsilon_3 \cos (\alpha' + \beta') \right\},$$

$$(\iota\omega) = \frac{\mu_1}{a_2} \left\{ 2 A \varepsilon_1 \cos \alpha - B \varepsilon_2 \cos (\alpha + \beta) \right\},$$

$$(\iota'\omega') = \frac{\mu_3}{a_3} \left\{ 2 A \varepsilon_2 \cos \alpha' - B \varepsilon_3 \cos (\alpha' + \beta') \right\},$$

from which

$$s. (\omega\omega) = \frac{\mu_1^2}{a_2^2} \left\{ 4 A^2 \varepsilon_1^2 + B^2 \varepsilon_2^2 - 5 A B \varepsilon_1 \varepsilon_2 \cos \beta \right\},$$

$$(\iota\omega)^2 = \frac{\mu_1^2}{a_2^2} \left\{ 4 A^2 \varepsilon_1^2 + B^2 \varepsilon_2^2 - 4 A B \varepsilon_1 \varepsilon_2 \cos \beta \right\}.$$

Therefore

$$s. \sigma = -\frac{\mu_1^2}{a_2^2} A B \varepsilon_1 \varepsilon_2 \cos \beta,$$

and similarly

$$s'. \sigma' = -\frac{\mu_3^2}{a_3^2} A B \varepsilon_2 \varepsilon_3 \cos \beta'$$

The only stable solutions are thus those in which β and β' are both 180° , and the only solution which satisfies this condition is (6). This solution, i. e. the case actually occurring in nature, is thus found to be the *only* stable periodic solution.

It needs hardly be mentioned that all the proofs given above suppose, that the developments in powers of ε_i and m_i converge so rapidly, that the sign of the various quantities used is determined by their first term. What the upper limits of ε_i and m_i are satisfying this condition, cannot be stated without a special investigation, but nature teaches us, that for the values occurring in the system of Jupiter the solution (6) still exists as a stable solution.

Physics. — “*Contribution to the theory of binary mixtures, XIII.*”

By Prof. J. D. VAN DER WAALS.

We have considered the closed curve, discussed in the preceding Contributions, as the projection of the section of two surfaces, viz. $\frac{d^2\psi}{dx^2} = 0$, and $\frac{d^2\psi}{dv^2} = 0$, constructed on an x -axis, a v -axis and a T -axis. Let the x -axis be directed to the right, the v -axis to the front and the T -axis vertically. The projection of these sections on the other projection planes will now also be a closed curve, in general

with a continuous course. We shall here chiefly consider the projection on the T, x -plane. This projection will possess a lowest and a highest point, and be enclosed on the right and on the left between a minimum and a maximum value of x , which two values of x are the same as those between which the v, x -projection is enclosed. But the highest and the lowest point of the T, x -projection is no special point in the v, x -projection. Only in this v, x -projection the points mentioned have the property that a line $\frac{d^2\psi}{dv^2} = 0$ and also a line $\frac{d^2\psi}{dx^2} = 0$ touches this v, x -projection at the minimum or the maximum temperature. At all temperatures between this minimum and this maximum temperature the v, x -projection is intersected by a line $\frac{d^2\psi}{dv^2} = 0$ in two points, and also by a line $\frac{d^2\psi}{dx^2} = 0$. But this contact can take place e. g. for the minimum temperature in a point that lies either on the left or on the right of the point in which v has the minimum value, and even, but in special cases, exactly in that point. So the quantity $\frac{dv}{dx}$ can be both positive and negative for the point in which T is maximum.

This holds also for the point where T is maximum, but generally the first mentioned point is of greater importance.

If for this first-mentioned point $\frac{dv}{dx}$ is positive, this is also the case with $\frac{dv}{dx}$ for the point in which $\frac{d^2\psi}{dv^2} = 0$ touches the closed curve, and as $\frac{d^3\psi}{dv^2 dx} + \frac{d^2\psi}{dv^3} \frac{dv}{dx} = 0$, the quantity $\frac{d^2\psi}{dv^2 dx}$ will be negative in the point in which T is minimum. In the same way the quantity $\frac{d^3\psi}{dx^3}$ is positive, and $\frac{d^2p}{dx^2}$ is positive for that point because also the line $\frac{d^2\psi}{dx^2} = 0$ touches, and so $\frac{d^3\psi}{dx^3} + \frac{d^2\psi}{dx^2} \frac{dv}{dx} = 0$, and the contact takes place in such a way that the whole closed curve lies inside $\frac{d^2\psi}{dx^2} = 0$. If the minimum temperature should just happen to be in the point of the closed curve where $\frac{dv}{dx} = 0$, we have at the same time

$\frac{d^2 p}{dx dv} = 0$ and $\frac{d^2 \psi}{dx^3} = 0$. If, on the other hand $\frac{dv}{dx}$ is negative, $\frac{d^2 p}{dx dv}$ is negative and also $\frac{d^2 \psi}{dx^3}$.

If the whole curve has contracted to a single point, this applies also to the two other projections — and for this case it is easy to express these projections in the value of ε_1 and ε_2 and n . Then, as was found before, $x = \frac{\sqrt{\varepsilon_1}}{n-1}$, and $1-x = \frac{n\sqrt{\varepsilon_2}}{n-1}$. Then the value of $\frac{v}{b}$ is equal to $\frac{1}{1-A}$ or equal to $1+B$, or $\frac{v}{b} = 1 + \frac{(n-1)^2}{n} \frac{\sqrt{\varepsilon_1} \sqrt{\varepsilon_2}}{(\sqrt{\varepsilon_1} + \sqrt{\varepsilon_2})^2}$ or $\frac{v-b}{b} = \frac{(n-1)^2}{n} \frac{\sqrt{\varepsilon_1} \sqrt{\varepsilon_2}}{(\sqrt{\varepsilon_1} + \sqrt{\varepsilon_2})^2}$. Both for $\varepsilon_1 = 0$ and for $\varepsilon_2 = 0$ is $v-b=0$, and as we have to do with a point lying on the line $\frac{dp}{dv} = 0$, $T=0$. A maximum value of v does not occur, but a maximum value of $\frac{v}{b}$ does. The easiest way to find this is by retaining the form:

$$\frac{v}{b} = 1 + B = 1 + \frac{(n-1)^2 x(1-x)}{(1-x+nx)^2}.$$

If v could be maximum, then:

$$\frac{db}{dx} + \frac{dB}{dx} = 0$$

or

$$\frac{n-1}{1+(n-1)x} + \frac{(n-1)^2 \frac{(1-x)^2 - n^2 x^2}{[1+(n-1)x]^4}}{1 + \frac{(n-1)^2 x(1-x)}{[1+(n-1)x]^2}} = 0.$$

After reduction we should find $n=0$. But the maximum value of $\frac{v}{b}$ or of $\frac{dB}{dx} = 0$ requires $nx = 1-x$ or $x = \frac{1}{n+1}$.

If for x and $1-x$ we put the value $\sqrt{\varepsilon_1}$ and $n\sqrt{\varepsilon_2}$, we find as condition $\varepsilon_1 = \varepsilon_2$; and so $p_{k_1} = p_{k_2}$. Then the value of $\frac{v}{b}$ is equal to $1 + \frac{(n-1)^2}{4n} = \frac{(n+1)^2}{4n}$. When n is small, $\frac{v}{b}$ is only little greater than 1, and so T' much smaller than T_k . But for very high values of n , e. g. about 10, the critical volume can be reached, and so T'

can be $= T_k$. With constantly rising value of n , the quantity $\frac{v}{b}$ can, indeed, increase indefinitely, in which, however, T becomes an ever smaller fraction of T_k . The value, however, which ε_1 and ε_2 will have, and consequently the value of x , $\frac{v}{b}$, and T , cannot be chosen arbitrarily. Besides that ε_1 and ε_2 must have such a value that the point denoted by them, lies on the parabola OPQ , the condition must also be fulfilled that $a^2_{12} = l^2 a_1 a_2$. For the case that $l^2 = 1$, the values of ε_1 and ε_2 are easy to calculate. Then the point $(\varepsilon_1, \varepsilon_2)$ must also lie on a second parabola, congruent with PQO , and shifted by an amount 1 along the ε_1 and ε_2 -axis in negative direction. These parabolae having their axes parallel, there will only be a single point of intersection. The equations which are to be satisfied, are then:

$$(\varepsilon_1 - n^2 \varepsilon_2)^2 = 4 n' (n - 1) (\varepsilon_1 - n \varepsilon_2)$$

and

$$(\varepsilon_1 - n^2 \varepsilon_2 + n^2 - 1)^2 = 4 n (n - 1) (\varepsilon_1 - n \varepsilon_2 + n - 1).$$

Then we find:

$$\sqrt{\varepsilon_1} = \frac{n+3}{4(n+1)}(n-1)$$

and

$$n \sqrt{\varepsilon_2} = \frac{3n+1}{4(n+1)}(n-1),$$

or $x = \frac{n+3}{4(n+1)}$ and $1-x = \frac{3n+1}{4(n+1)}$. The value of T obtained in this case is smaller than the one calculated above if we take $\varepsilon_1 = \varepsilon_2$. If $l^2 < 1$, ε_1 increases, of course, and ε_2 decreases and reversely. A value of l^2 might be chosen so that T assumes a maximum value, but to this we come back later on. But in any case the values of ε_1 and ε_2 may be such that the two surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2}$ touch only at one single temperature, without intersecting further. And if n is not very large, this temperature lies very low. Thus from

the formula $MRT = 2 \frac{a}{b} \frac{\left(\frac{v-b}{b}\right)^2}{\left(\frac{v}{b}\right)^3}$ and the supposition $l^2 = 1$ we calculate

for $n = 2$ the value of $\frac{T}{T_k} = \frac{1}{14}$ about, and for other values

of l^2 this value of $\frac{T}{T_k}$ becomes but little higher. But ε_1 and ε_2 might be such for higher value of n , that v approaches to $3b$ and T to T_k ; this might be the case for $n = 10$. So we see here the following possibilities for the phenomena of non-miscibility, dependent on the value of n . For low value of n , contact of the said two surfaces may take place at so low a temperature that observation is impossible on account of the occurrence of the solid state. For increasing value of n this temperature rises, and for a certain value of n , it may have risen to $\frac{1}{3}$, or $\frac{1}{2}$ T_k and so the observation will no longer be prevented by the appearance of the solid state. As, if contact takes place of the two surfaces at certain temperature, two plaitpoints make their appearance already at lower temperature, which vanish again at higher temperature than that of the contact, three-phase-pressure will exist between two temperatures. A precise determination of the value of n at which this is the case, is not possible, if it were only on account of the fact that we have not been able to determine what relation exists between the temperature of contact and that at which the double plaitpoint begins to appear or disappears, and moreover because we have not been able to determine how long the double plaitpoint must have been present before the plaitpoint appears or disappears on the binodal line. But for small value of n the lowest temperature at which non-miscibility sets in, can certainly not be observed, at least not if the cause of non-miscibility is to be ascribed to the circumstance discussed here.

So in the T, x -projection there is only a single point for which the value of x will be found in the left half, in the case discussed here. But if we besides draw the T, x -projection of the plaitpoints which are the consequence of the existence of the point of contact of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, we obtain again a closed curve. Probably the projection of the point of contact lies, especially as regards the value of x , very eccentrically with regard to this curve — possibly even to the right outside it. The lefthand branch of this curve is the projection of the unrealisable plaitpoints, and these will always have considerably moved to smaller values of x . But if the projection is a closed curve, they must rapidly approach the points of the righthand branch at higher temperature. However, another case may be expected. In the case that the projection of the plaitpoints remains below the curve indicating the course of T_k , the closed curve is to be expected — but if the value of T should rise so high that the curve $T_k = f(x)$ would be cut, the lefthand branch of the projection would meet the ordinary plaitpoint, which approaches from the side of the component

with the lowest value of T_1 . The result is then that the projection of the plaitpoints forms a curve which begins at $x = 0$ and $T = T_{k_1}$, rises from there to the highest double plaitpoint temperature, then falls to the lowest plaitpoint temperature, and ascends again from there to T_{k_2} . This last case has been treated more extensively These Proc. Vol. VII. The transformation of a branch plait etc.

Figure 39 gives a schematic representation of the T, x -projection for the first case. The point P represents the point of contact of the two surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$. The full line represents the locus of the plaitpoints, the point P_{ab} is the lowest double plaitpoint, and P_{cd} is the highest. In the points Q_1 and Q_2 the realisable plaitpoint appears or disappears on the binodal line — and then there is three-phase-pressure between the temperatures of Q_1 and Q_2 . The dotted curve, which has its lowest and its highest

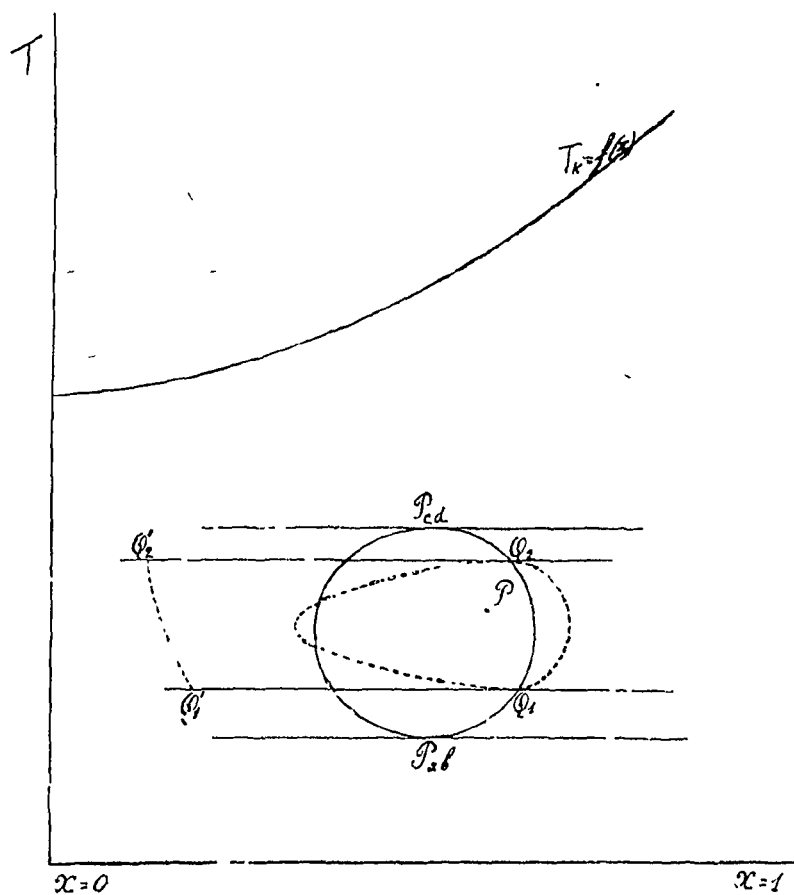


Fig. 39

point in Q_1 and Q_2 , denotes the concentrations of the coexisting liquid phases at every T , and the curve Q_1, Q_2 indicates the concentration of the third coexisting phase (vapour phase). The curve $T_k = f(x)$ has been drawn higher in the figure.

It follows, however, from the remark, Contribution XI, p. 440, Vol. XI, that the point P need not even be present, and that yet the remaining part of the figure, but then between narrower temperature limits, may continue to exist. We might even imagine the circumstances to be such that the points P_{ab} and P_{cd} coincide, but then Q_1 and Q_2 and Q'_1 and Q'_2 would have coincided already before.

The second case is represented in fig. 40. Again P is the projection on the T, x -plane of the point of contact of the two surfaces $\frac{d\psi^2}{dx^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. The full curve $A Q_2 P_{cd} P_{ab} Q_1 B$ etc. is that of the

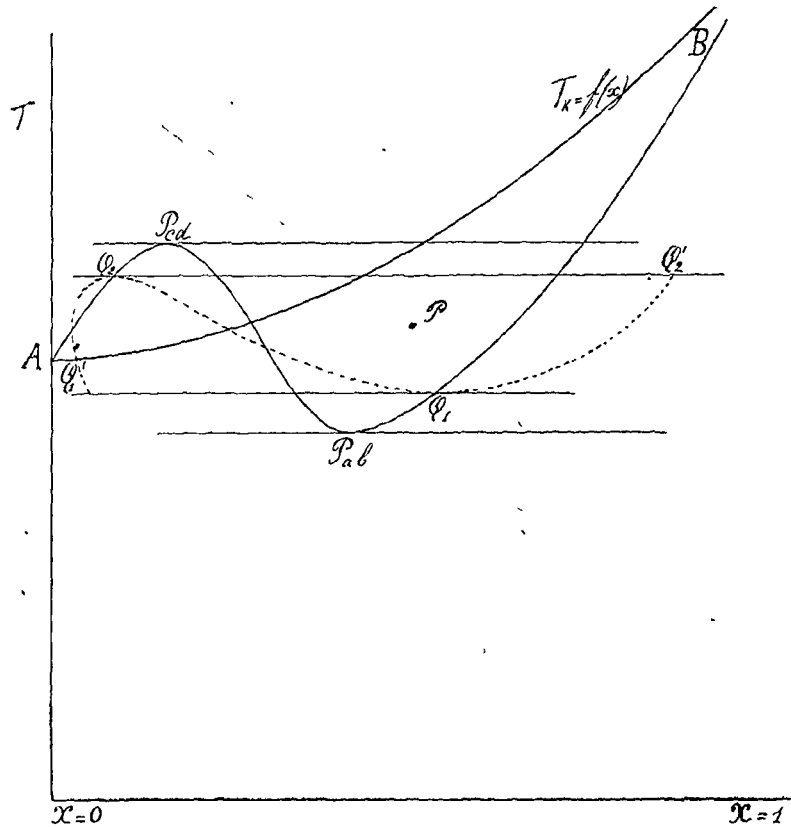


Fig. 40.

plaitpoints. The points P_{ab} and P_{cd} are the double plaitpoints. So

there are three plaitpoints between the temperature of A , viz. T_{k_1} , and that of P_{cd} , unless P_{ab} should lie higher than A , in which case P_{ab} would take the place of T_{k_1} . The curve $T_k = f(x)$ is also inserted in the figure. It will have to intersect the plaitpoint curve at $x < 1$, and that twice. The first point has not been indicated by a special mark, but the second point of intersection is supposed to be in the neighbourhood of B . If we draw a p, x -section of the surface of saturation, and add to it a line indicating the pressure at which there would be coexistence if the mixture behaved as an homogeneous substance, the extreme point of this line would lie at the same value of x as that of the plaitpoint, at the value of T of the second point of intersection just mentioned.

For higher value of T we have then again the rule that for a given mixture $T_{pl} > T_k$, which is generally considered as the normal case. This being really the case for x very small, and x nearly 1, when there is intersection of the curves $T_k = f(x)$ and $T_{pl} = \varphi(x)$, this will have to take place twice. For the points Q_1 and Q_2 the plaitpoint lies on the binodal line, and between the temperatures Q_1 and Q_2 there is three-phase-pressure. The concentration of the three coexisting phases is indicated by the dotted line $Q'_1 Q_2 Q_1 Q'_2$. We might call the part $Q'_1 Q_2$ of this line the vapour branch. The vapour branch presents a particularity in the drawing which has escaped attention so far, viz. that it can contain a point in which x has a minimum value. I have not drawn this particularity in the vapour branch of fig. 39, because it is less probable there. This applying to a circumstance which has not been noticed as yet, and which is yet not devoid of importance, a digression to show the possibility of the existence of such a point with minimum value of x , may be useful. The more so, because in the discussion properties will be mentioned the knowledge of which is necessary if we want to understand the full meaning of different particularities occurring for the three-phase-pressure.

Let us call the concentration of the point representing the vapour phase, x_1 , and let x_2 and x_3 denote the concentrations of the liquid phase — and let us put $x_1 < x_2 < x_3$. Now the following equations hold:

$$v_{21} dp = (x_2 - x_1) \left(\frac{d^2 \xi}{dx_1^2} \right)_{pT} dx_1 + \eta_{21} dT$$

and

$$v_{31} dp = (x_3 - x_1) \left(\frac{d^2 \xi}{dx_1^2} \right)_{pT} dx_1 + \eta_{31} dT.$$

For the three-phase-pressure both equations hold, and we get the value of $\frac{dp}{dT}$ for this three-phase-pressure which we shall indicate by $\frac{dp}{dT_{123}}$, by eliminating dx_1 from these two equations. If we divide the first equations by $x_2 - x_1$, and the second by $x_3 - x_1$, and if we subtract the quotients from each other, we get the well-known formula :

$$\frac{dp}{dT_{123}} = \frac{\frac{\eta_2 - \eta_1}{x_2 - x_1} - \frac{\eta_3 - \eta_1}{x_3 - x_1}}{\frac{v_2 - v_1}{x_2 - x_1} - \frac{v_3 - v_1}{x_3 - x_1}}$$

If we substitute this value of $\frac{dp}{dT_{123}}$ in the two equations given we get :

$$v_{21} \frac{dp}{dT_{123}} = (x_2 - x_1) \left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \frac{dx_1}{dT} + \eta_{21}$$

and

$$v_{31} \frac{dp}{dT_{123}} = (x_3 - x_1) \left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \frac{dx_1}{dT} + \eta_{31}$$

After division by v_{21} and v_{31} , we may also write :

$$\frac{dp}{dT_{123}} = \frac{\left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \frac{dx_1}{dT}}{v_{21}} + \left(\frac{\partial p}{\partial T} \right)_{x_{21}}$$

and

$$\frac{dp}{dT_{123}} = \frac{\left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \frac{dx_1}{dT}}{v_{31}} + \left(\frac{\partial p}{\partial T} \right)_{x_{31}}$$

or

$$\frac{dp}{dT_{123}} = \left(\frac{dp}{dx_1} \right)_T \frac{dx_1}{dT} + \left(\frac{\partial p}{\partial T} \right)_{x_{31}}$$

if we represent by $\left(\frac{dp}{dT} \right)_{x_{21}}$ and $\left(\frac{dp}{dT} \right)_{x_{31}}$ the ratio of the increase of p and the increase of T on the vapour sheet of the surface of saturation for a section with constant value of $x = x_1$, respectively for the coexisting equilibrium between the phases 1 with 2, and 1 with 3. So the difference $\frac{dp}{dT_{123}} - \left(\frac{dp}{dT} \right)_{x_{21}}$, multiplied by $\frac{v_{31}}{x_2 - x_1}$

indicates the sign of dx_1 . In the same way if we change 2 into 3. Now it is true that the surface of saturation has been greatly modified by the existence of the three-phase-pressure. But this modification is restricted to values of T , between those at which this pressure begins and ends, and also within these limits of temperature, the surface of saturation consists only of a lower sheet and an upper sheet, if we leave the metastable and unstable coexisting phases out of account. So every section for given value of x , is again, except for the modifications inside the said limits of temperature, the well-known figure in which the lower branch passes continuously into the upper branch. Let us now think the line $p_{1,2,3}$ as function of T traced in every section. Only for so far this line lies between the upper and the lower branch of the section of the modified surface of saturation, the mixture of the chosen value of x can split up into three phases. If this line intersects either the upper branch, or the lower branch, and if therefore part of the line $p_{1,2,3}$ lies outside the surface of saturation, this must be considered as a parasitic branch, at least for the mixture chosen. So the dotted lines of fig. 39 and fig. 40 represent the values of T for which the line $p_{1,2,3}$ intersects a chosen section of the surface of saturation. And so the question whether in fig. 40 the situation of point Q'_1 is such that another point occurs in the dotted curve for this value of x , coincides with the question whether there exist sections for which the line $p_{1,2,3}$ intersects the saturation curve twice. As $\frac{V_{21}}{x_2 - x_1}$ and $\frac{V_{31}}{x_3 - x_1}$ are negative on the vapour branch according to the formula for the calculation of $\frac{dx_1}{dT}$ a negative value of this quantity is attended with a positive value of $\frac{dp}{dT_{123}} - \left(\frac{dp}{Td}\right)_x$ or with the line $p_{1,2,3}$ entering the heterogeneous region with increasing T . Reversely a positive value of $\frac{dx}{dT}$ shows that the line $p_{1,2,3}$ enters the homogeneous region with increasing temperature, and therefore appears further only as parasitic branch. Now in the point Q'_2 the value of $\left(\frac{dp}{dT}\right)_{123}$ is equal to the value of $\left(\frac{dp}{dT}\right)_2$, as it is on the section of the surface of saturation for the x of the point Q_1 , as follows if in the formula for $\frac{dp}{dT_{123}}$ we put $x_2 + dx_2$ for x_3 , $V_2 + dV_2$ for V_3 , and $\eta_2 + d\eta_2$

for η_3 . Then we find namely

$$\frac{dp}{dT_{123}} = \frac{\eta_1 - \eta_2 - (x_1 - x_2) \frac{d\eta_2}{dx_2}}{v_1 - v_2 - (x_1 - x_2) \frac{dv_2}{dx_2}}$$

For $\frac{d\eta_2}{dx_2}$ and $\frac{dv_2}{dx_2}$ we may write $\left(\frac{d\eta_2}{dx_2}\right)_{pT}$ and $\left(\frac{dv_2}{dx_2}\right)_{pT}$ because the phases 2 and 3 then have equal p and T . Now the point Q_1 is a liquid phase, and so a point of the upper sheet of the surface of saturation. In general the value of $\left(\frac{\partial p}{\partial T}\right)_x$ for such a point is not great at low temperatures. But yet it is larger on the whole than the value of $\left(\frac{\partial p}{\partial T}\right)_x$ on the vapour sheet, even for sections for which x is smaller. At least for temperatures which lie pretty far from T_k , so that there are therefore two possibilities chiefly dependent on the temperature: either the value of $\left(\frac{\partial p}{\partial T}\right)_x$ in the point Q_1 may be larger than $\left(\frac{\partial p}{\partial T}\right)_x$ for the point Q'_1 , or smaller — and so the value of x for the point Q'_1 may either run back or proceed.

Over the full width of the three-phase-curve on the right of Q_2 the line p_{123} leaves the upper sheet of the surface of saturation with rising temperature. This is also still the case for points on the left of Q_2 ; but a point will soon occur where the three-phase-curve passes to the lower sheet. So this point must lie on the “contour apparent” with regard to the T, x -surface; or in other words: it must be a critical point of contact. Then too the three-phase-curve still passes to smaller value of x . And only afterwards a point can occur where x has minimum value, but this only on the lower sheet. And if the temperature of Q is comparatively low, the vapour branch of the three-phase-curve will certainly run again to the right with falling temperature. Accordingly I have drawn the vapour branch in fig. 39 in this way, though there too the circumstance may occur that x runs back. Besides, the circumstance occurs there that x shows minimum and maximum value for the liquid phases. The condition for x , whether maximum or minimum is $\left(\frac{\partial p}{\partial T}\right)_{x_2} = \left(\frac{\partial p}{\partial T}\right)_{x_1} = \frac{dp}{dT_{123}}$, if we denote the phase where x runs back, by 1.

But let us return after the discussion of these particularities, to the treatment of the T, x -projection of the closed curve.

We have already observed that the point P is not found when the surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect. Reversely P extends to a curve if the surfaces do not only touch, but intersect. We obtain the equation of this closed curve, if we solve the value of $\frac{v}{b}$ from the equation:

$$\frac{v}{b}(1-A) - 2\frac{v}{b} + (1+B) = 0$$

and substitute it in $\frac{d^2\psi}{dx^2} = 0$ or $\frac{d^2\psi}{dv^2} = 0$. It is simplest to do this in

$$\frac{d^2\psi}{dv^2} = 0, \text{ or } MRT = 2\frac{a}{b} \frac{\left(\frac{v-b}{b}\right)^2}{\left(\frac{v}{b}\right)^3}; \text{ or to substitute the value of}$$

$\frac{b}{v}$ in $MRT = 2\frac{a}{b} \left(\frac{b}{v}\right) \left(1 - \frac{b}{v}\right)^2$. If we write $\frac{b}{v}$ in the following form:

$$\frac{b}{v} = \frac{1 \mp \sqrt{A-B+AB}}{1+B} = \frac{1 \mp \sqrt{X}}{1+B}$$

and

$$1 - \frac{b}{v} = \frac{B \pm \sqrt{A-B+AB}}{1+B} = \frac{B \pm \sqrt{X}}{1+B}$$

we find:

$$MRT = 2\frac{a}{b} \frac{(B^2 - 2BX + X) \pm (2B - B^2 + X)\sqrt{X}}{(1+B)^3} \quad \dots (1)$$

When $X = A - B + AB = AB \left\{ \frac{1}{B} - \frac{1}{A} + 1 \right\}$ is positive, T is real, and there are two values of T for every value of x . For the same values of x for which in the v, x -projection the two values of $\frac{v}{b}$ coincide, the two values of T coincide in the T, x -projection. The values of T assume a simple form for these limiting values of x , because then $X = 0$, i.e. $MRT = 2\frac{a}{b} \frac{B^2}{(1+B)^3}$; of course this value must also hold for the case that these limiting values of x coincide, which we treated above. We can even simplify this form

of MRT for the calculation and obtain the form:

$$MRT = \frac{2c}{b_1(n-1)^2} [1 + (n-1)x] \frac{1}{\left\{ \frac{1}{(n-1)^2} \frac{1}{x} + \frac{n^2}{(n-1)^2} \frac{1}{1-x} \right\}^2}$$

by writing $b \frac{1}{\frac{1}{a}} = b \frac{x(1-x)}{\frac{1}{a}} = \frac{cb}{\left(\frac{db}{dx}\right)^2} \frac{B}{A}$ for $\frac{v}{b}$.

If we seek the maximum value of T , we find for the determination of x an equation of the 3^d degree, viz.:

$$(1-x)^3 + x(1-x)^2 \frac{3n-1}{2} - n^2 x^2 \frac{3-n}{2} - n^3 x^3 = 0$$

and putting $\frac{nx}{1-x} = k$:

$$1 + k \frac{3n-1}{2n} - k^2 \frac{3-n}{2} - k^3 = 0.$$

For $n=1$ we should have $k=1$, for $n=2$ $k=1,22$; but for very high value of n $\frac{k}{n}$ approaches to $\frac{1}{2}$. This implies that for $n=1$ the maximum value of MRT lies at $x=\frac{1}{2}$, and for $n=\infty$ at $x=\frac{1}{3}$.

For all other values of n x lies between $\frac{1}{2}$ and $\frac{1}{3}$. By the aid of this value of x we can then calculate the highest value of MRT for the points where $X=0$. But the conclusion is not different from that at which we arrived above: viz. that only with n appreciably larger than 3 the value of the temperature can rise to T_k or even to T_{k_1} .

The value which we found in general in equation (1) for the temperature of the points of the closed curve is too intricate to be fully discussed. We can, however, foresee what in general the shape of the T,x -projection will be. For a curve of small dimension the point P of fig. 39 and fig. 40 is to be replaced by a smaller closed curve which extends according as the former curve itself assumes greater dimensions. Of course the other lines experience the influence of this. Thus in fig. 39 the point P_{ab} will descend and P_{cd} ascend: For every value of x , so of a , b , B and X , the first part of MRT in equation (1), viz.: $2 \frac{a}{b} \frac{B^2 + X(1-2B)}{(1+B)^2}$ indicates the value of the arith-

metrical mean, so half the sum of the lowest and the highest temperature; and the second part, viz. $2 \frac{a}{b} (2B - B^2 + X) \sqrt{X}$ denotes the amount that the really occurring temperatures lie above or below this middle value. This second part is imaginary outside the limiting values of x . For between these limiting values of x , X is positive, and beyond them negative — but the first part exists over the full width. The course of this first may be given in the main points. Beginning with $T=0$ and $x=0$ it ends also with this value at $x=1$. But for very small value of x or $1-x$, provided it be outside the limiting values of x , this first part is negative.

For the limiting values of x , where $X=0$, it has the above treated positive value $MRT = 2 \frac{a}{b} \frac{B^2}{1+B^2}$. But just beyond these limiting values of x a value equal to 0 must occur; we conclude to this by noticing that if x or $1-x$ is very small, B^2 and XB may be neglected by the side of B , while X is negative beyond the limiting value of x . The curve which represents the first part begins with an ordinate equal to zero, then descends below the axis, but intersects the axis again before the smallest value of x is reached for which X is equal to zero, then rises to a maximum value, after which it descends below the axis, and finally terminates with a value zero.

So if we draw the curve T_k as in fig. 39, this curve is of course the limit above which T cannot rise for any point of the closed curve. The closed curve being the section of two surfaces which have each a "contour apparent" on the T, x -plane, the projection of the sections cannot fall outside this outline. So the T, x -projection can have either one or two points in common with the curve T_k , in which points it must touch this curve. In these points of contact $\frac{v}{b} = 3$.

If there are two points of contact $\frac{v}{b}$ is > 3 between these points.

The observation that $\frac{v}{b} = 3$ in the points of contact enables us to show that this circumstance cannot occur for low value of n . First of all not for $n < 2$, because, as we saw before, v must there be smaller than $b_2 = 2b_1$. If we introduce into the equation:

$$\left(\frac{v}{b}\right)^2 (1-A) - 2 \frac{v}{b} + (1+B) = 0$$

the condition $\frac{v}{b} = 3$, we get:

$$4 = 9A - B.$$

Now

$$B = \frac{1}{\frac{1}{(n-1)^2 x} + \frac{1}{(n-1)^2 (1-x)} - 1},$$

and A

$$= \frac{1}{\frac{1+\varepsilon_1}{(n-1)^2 x} + \frac{n^2(1+\varepsilon_2)}{(n-1)^2 (1-x)} - 1}.$$

- Let us take two extreme cases: 1. the case that ε_1 and $\varepsilon_2 = 0$;
 2. the case that $\frac{\varepsilon_1}{(n-1)^2 x} + \frac{n^2 \varepsilon_2}{(n-1)^2 (1-x)} = 1$.

In the first case $B = A$, and so $B = \frac{1}{2}$, or it must be possible to

find real values for x from the equation: $\frac{1}{(n-1)^2 x} + \frac{n^2}{(n-1)^2 (1-x)} = 3$,
 which values must, moreover, lie between the limiting values of x ,
 in this case $x = 0$ and $x = 1$. For the roots to be real

$$1 \text{ must be } > \frac{\sqrt{\frac{1}{3}}}{n-1} + \frac{n \sqrt{\frac{1}{3}}}{n-1}$$

or

$$\frac{n+1}{n-1} < \sqrt{3}$$

or

$$n > \frac{\sqrt{3}+1}{\sqrt{3}-1};$$

if the sign $>$ is changed into $=$, there is only one root at

$$n = \frac{\sqrt{\frac{1}{3}}}{n-1} \text{ and } 1-x = \frac{n}{n-1} \sqrt{\frac{1}{3}}. \text{ So for } n \text{ about } 3.75 \frac{v}{b}$$

$= 3$ for $x = \frac{1}{4.75}$, if $\varepsilon_1 = \varepsilon_2 = 0$. Then the closed curve touches the

curve T_k in the T, x -projection. But then the lower branch of the T, x -line will have descended to $T = 0$. Then we have to expect fig. 40, however with this modification that P_{ab} lies at a height $= 0$ and the three-phase-pressure is already found at all low temperatures.

In the second case, in which the supposition $\frac{\varepsilon_1}{(n-1)^2 x} + \frac{n^2 \varepsilon_2}{(n-1)^2 (1-x)} = 1$

however, involves the assumption that the point for which $\frac{v}{b} = 3$,

lies at a value of x which is just one of the limiting values of x ,

$\frac{B}{1+B} = A$ and the equation $4=9A-B$ yields the value 2 for B .

So $\frac{1}{(n-1)^2 x} + \frac{n^2}{(n-1)^2} \frac{1}{1-x} = \frac{3}{2}$ must then yield real values for x , and

so $\sqrt{\frac{3}{2}}$ must be $> \frac{n+1}{n-1}$, or $n > 10$.

Now, however, if we assign values to ε_1 and ε_2 the condition of the second case will in general not be fulfilled, and

$\frac{\varepsilon_1}{(n-1)^2} \frac{1}{n} + \frac{n^2 \varepsilon_2}{(n-1)^2} \frac{1}{1-x}$ will not have risen to 1 — but we shall

have to put $\frac{\varepsilon_1}{(n-1)^2} \frac{1}{n} + \frac{n^2 \varepsilon_2}{(n-1)^2} \frac{1}{1-x} < 1$, or equal to $1-\alpha$, in which

α will have a value between 1 (that of the first case), and 0 (that of the second case). And the result will then be that the condition

$\frac{v}{b} = 3$ will require a value of n which is greater than 3.75, but

which need not rise to 10.

But I shall not continue the calculations required for this. If we review what precedes, it appears sufficiently: 1 that the case that three-phase-pressure exists between temperatures that differ little, may occur for all values of n — but that if n is small, these two temperatures lie too low to be observed. It is not possible to give the exact value of n for which these temperatures if they exist, can be observed, before the ratio is known between the temperature at

which the two surfaces $\frac{d^2 \psi}{dx^2} = 0$ and $\frac{d^2 \psi}{dv^2} = 0$ touch, and the temperature at which the double plaitpoint has appeared or disappears.

2. That for the case of fig. 40 the required value of n may be estimated as at least 4. 3. That as ε_1 and ε_2 descend below the parabola OPQ , the two temperatures between which three-phase-pressure can exist, diverge further, and that only if ε_1 and ε_2 (we only deal with positive ε_1 and ε_2 here) have become equal to 0, the lowest temperature has descended to the absolute zero point.

If we further take into consideration that the point $\varepsilon_1, \varepsilon_2$ lies on the curve $a^2_{12} = b^2 a_1 a_2$, which represents in ε_1 and ε_2 an ellipse, a parabola or a hyperbola according as $b^2 < 1$ or > 1 , and that of this curve only those points which lie in the triangle OPQ (below the parabola) yield a closed curve which we have treated, we see that the phenomena discussed do not only depend on n , but that besides special relations must exist for a_1 and a_2 and a_{12} , which are

represented by ε_1 and ε_2 , positive in the equations $\frac{a_1}{c} = \frac{1 + \varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c} = \frac{n^2(1 + \varepsilon_2)}{(n+1)^2}$ and $n-1 > \sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2}$. By far the greater part of the curve $a^2_{12} = l^2 a_1 a_2$ lies outside this region, and the occurrence of the discussed phenomena will, therefore, have to be considered as comparatively rare. If we descend in the region $\hat{O}PQ$, so that either ε_1 or ε_2 , or both become negative, then (but the consequence of a negative value of ε_1 and ε_2 has not yet been discussed) three-phase-pressure is to be expected already at $T=0$. If we go upwards along the curve $a^2_{12} = l^2 a_1 a_2$, and if we get above the parabola with ε_1 and ε_2 , there is perfect miscibility. (For the values of ε_1 and ε_2 required for perfect miscibility consult Contribution XI p. 443). As the upward movement along the curve $a^2_{12} = l^2 a_1 a_2$ is attended with decrease of $\frac{pk_2}{pk_1}$, it follows from this that if in analogous cases the ratio $\frac{pk_2}{pk_1}$ decreases, we pass from non-miscibility to perfect miscibility.

The conclusions in the derivation of which we have supposed to treat only normal cases, viz. such for which no chemical action takes place between the two components, or for which each of the components behaves normally, are quite corroborated by the observations. I know only of one exception, namely that the case of fig. 40 occurs also in the observations of KUENEN for mixtures of ethane and aethyl-alcohol, etc. In this case we have to put n either below or just above 2. How it is that the abnormal behaviour of alcohol has here an influence as if n were increased, cannot be accounted for as yet. But in the cases of BÜCHNER for mixtures of carbonic acid and organic liquids, for which also fig. 40 gives the course schematically, n will, no doubt, have the value found by calculation. (BÜCHNER, Thesis for the doctorate 1905).

In conclusion a few remarks.

1. In fig. 30 of Contribution VI I have already given the course of the plaitpoint line for the case of fig. 39, and also of the three-phase-pressure of T .

2. The upper and the lower sheet of the surface of saturation are subjected to some modification in the case of fig. 39 only between the two temperatures between which there is three-phase-pressure. The modification for the upper sheet consists in what follows. Between the limiting values of x of the dotted closed curve of fig. 39 the

upper sheet is raised. At the limiting values of x this rise is still equal to zero.

But for values of x , which differ from these limiting values, the rise assumes certain values, at first, however, only between temperatures which differ little. But this is accurately rendered by fig. 39. The consequence of all this is that if a certain increase of pressure is applied, e. g. if we observe above the maximum pressure of the modified liquid sheet, the total non-miscibility has disappeared. If we lower the pressure, the non-miscibility may reappear but at a pressure which is only slightly less than the maximum pressure it exists only over a very small range of temperature. In other words there the dotted curve of fig. 39 has greatly contracted. In this two cases will no doubt occur, either real minimum pressure occurs, or the pressure in the point Q is the highest. At higher temperatures, however, splitting up into vapour and liquid is still possible.

3. If in fig. 40 the circumstance occurs of minimum value of x on the vapour branch, there exists for some mixtures, if we take care to follow the three-phase-pressure, retrogression of the condensation.

For the mixtures which show the above discussed non-miscibility between two temperatures, both a_{12}^2 may be $> a_1 a_2$, and a_{12}^2 may be $< a_1 a_2$. However if $a_{12}^2 > a_1 a_2$, the chance to non-miscibility is smaller. In this case the points $\varepsilon_1, \varepsilon_2$ lie on a hyperbola which intersects the space OPQ below the parabola close to the point Q ; and as the intersection takes place nearer to Q , the distance between the parabola and the ε_2 -axis is smaller. And as soon as the value of $\frac{a_{12}^2}{a_1 a_2}$ would become so large that the intersection of the hyperbola with the ε_2 -axis takes place past Q , non-miscibility will be quite excluded. So if $\frac{a_{12}^2}{a_1 a_2} > \frac{1}{4} \frac{(n^2+1)^2}{n^2+(n-1)^2}$. For the full discussion of the intersection of the surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ it now remains to examine the cases with negative values of ε_1 and ε_2 .

(March 25, 1909).