Physics. — *"Contribution to the theory of the binary mixtures XVI."* By Prof. J. D. VAN DER WAALS.

In the Proceedings of Oct. 1911, p. 421 Prof KUENEN says that he cannot agree with the view that in the point in which a plait splits off from the transverse plait, the value of $\left(\frac{d^2v}{dx^2}\right)_p$ should be equal to 0.

The equality $\left(\frac{d^2v}{dx^2}\right)_{bin} = \left(\frac{d^2v}{dx^2}\right)_p$ he admits as valid, but he objects to the assumption that the double point at the same time would be a point of inflection of an isobar. Now in the double point the equality, which he wants to maintain, has strictly speaking ceased to exist. In such a double point $\left(\frac{d^2v}{dx^2}\right)_{bin}$ is infinitely great, because there the binodal curve consists of two line elements, which enclose an acute or an obtuse angle. But leaving this aside as self-evident, it seems of importance to examine whether his opposition to $\frac{d^2v}{dx^2}_p = 0$ is well-founded. This equation has namely enabled me to indicate the place where such a splitting up is possible — and it has even been one of the reasons which led me to examine where points of inflection can occur in the isobars and to occupy myself with the locus of these points of inflection [1]).

KUENEN thinks he can justify his objection to the theorem that in the said double point $\frac{d^2v}{dx^2}_p = 0$ by the observation that this splitting up is assumed to take place *inside* the binodal curve. And this observation is by no means conclusive. Inside the binodal curve the surface is only partly unstable — there is also a stable part, in which the surface seen from below, is convex-convex. And for the circumstance that the splitting up be such that in the double point $\frac{d^2v}{dx^2}_p = 0$, it is now only required that it lie (to express it briefly) on the convex-convex part of the surface — or expressed more sharply, that a moment after the splitting up there exist a convex-convex part between. The very consideration that properties of the

[1]) If the four branches of the binodal curve in the double point are reduced to two branches, $\left(\frac{d^2v}{dx^2}\right)_{bin} = \left(\frac{d^2v}{dx^2}\right)_p$ can be maintained also in the double point and we are naturally led to the insight that the value is there =0.

surface at that place must decide about the possibility of the existence of the assumed splitting up, whereas the position of the binodal curve is also determined by properties of the surface in sometimes very remote parts, makes us see that the circumstance whether a point lies inside or outside the binodal line, cannot be decisive.

The first, and I think I may say the well-known case of such a splitting up of a plait, occurs for mixtures with a minimum value of T_k (for mixtures taken as homogeneous). In this case also the binodal curve of this transverse plait splits up, and both parts of these binodal lines can be realised. But it is by no means an absurdity to suppose that in consequence of properties of the surface in parts lying very far to the left this double point was covered, and unrealisable. Then the binodal curves at the temperature at which the splitting up takes place would be quite different ones and the already existing one would also have remained covered for a great part.

That at this well-known splitting up $\frac{d^2v}{dx^2_p} = 0$ in the double point, is, I think, also accepted by KUENEN, — and the admission that after the splitting up the plaitpoints lie in such a way that for one $\left(\frac{d^2v}{dx^2}\right)_{bin}$ is positive and for the second negative, leads to the conclusion that in the double point $\frac{d^2v}{dx^2_p}$ must necessarily be equal to 0. Such a splitting up of a transverse plait into a righthand side and a left-hand side exists and can be demonstrated experimentally for a number of mixtures. Now for an explanation of other phenomena I was confronted by the question whether a plait could also split up in such a way that after the splitting up there can be question of an upper and a lower part — or rather in a part with greater and in one with smaller volumes. That in this respect experimental investigation is still very incomplete, is readily admitted.

Now with regard to the place of the double point three different suppositions can be made; 1. outside the binodal curve of the transverse plait; 2. inside the binodal curve; 3. just on the binodal curve. At the temperature at which the splitting up takes place (T_{sp}) the transverse plait still extends over the whole breadth.

In the first case the splitting up can be observed experimentally. If we inquire into the properties of the binodal curve for the equilibrium liquid-liquid and liquid-vapour, we get 1. in the double point two intersecting curves, 2. the already existing liquid branch of the transverse plait, of course slightly modified, and running through the unstable part of what I will call longitudinal plait.

At somewhat higher temperature, so above that of the splitting up, the convex-convex part of the ψ-surface has made its appearance in the double point — a separate curve has split off either quite closed or open towards the side of the limiting volumes, concerning which I refer to former observations. And moreover the transverse plait has got a branch plait with a plaitpoint at the side of the small volumes. To close this branch plait a hidden plaitpoint is required — also in reference to this I may refer to former communications. At still higher temperature the branch plait has retreated more and more towards the transverse plait; the plaitpoint reaches the binodal curve of the transverse plait, and then the liquid branch of this binodal no longer runs through an unstable region.

But, and for this I also refer to former investigations, then too the hidden plaitpoint still exists. And not before the temperature is still higher does the hidden plaitpoint unite with the plaitpoint of the branch plait that existed before. From the temperature at which this plaitpoint lay on the binodal curve there existed inside the binodal curve a pair of *heterogeneous* plaitpoints. But strictly speaking if we do not confine ourselves to that part of the surface lying inside the transverse plait, there exists such a pair of heterogeneous plaitpoints already at T_{sp}. And if the longitudinal plait on the side of the small volumes is closed, there exists such a pair of plaitpoints already before the splitting up. Only then at the spitting up all at once substitution of quite another point takes place for one of the points belonging to the pair of plaitpoints, to which subject I shall return in a following communication.

This first case for the place which may be possible for the double point, is not known, and is certainly not realized in the mixture examined by VAN DER LEE. And now it was my purpose to explain the 2nd case in Contribution XV.

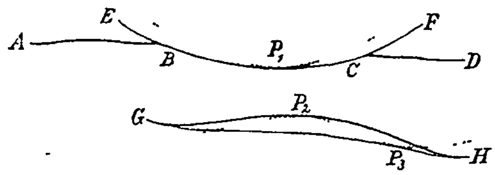
Not that there is a great difference with what I described above — there is only a difference as far as the place of the double point is concerned.

This double point might happen to lie exactly on the binodal curve of the transverse plait, which I have referred to above as the third case. This would certainly have to be called a coincidence. As I remarked above the property of the surface which leads to splitting up, and the property on the vapour side of the transverse plait which governs the place of the binodal curve of the transverse plait to a high degree, would have to answer very special demands. I consider the chance that this takes place as about zero.

Moreover the difference between this particular case and the 2nd

is so slight that if the latter has been discussed, also the particularities of the particular case are easily seen.

In the adjoined figure I have represented the position of the spinodal and binodal curves at a temperature somewhat above T_{sp}. AB and CD denote two portions of the binodal curve of the transverse plait, for so far it is to be realized. EBP_1CF represents the binodal curve of that part of the longitudinal plait that has split off



and moves towards smaller volumes at rising temperature. P_1 is the plaitpoint moving towards smaller volumes. By P_2 the plaitpoint moving to greater volumes is represented. At T_{sp} P_1 and P_2 coincide. But now we know from former considerations and I refer among others to these Proc. VIII p. 184 that there must also still exist a closed binodal curve, of which P_2 is a plaitpoint, and that there must be found one more (third) plaitpoint to close this binodal curve. The points P_2 and P_3 together form a pair of heterogeneous plaitpoints. At T_{sp} this hidden plaitpoint already exists, but P_2 and P_3 do not coincide until at a temperature that lies higher (but how much higher cannot be indicated here any more than in the cited paper).

At a temperature above that for which the above figure holds, the longitudinal plait moving to smaller volumes has the plaitpoint P_1 on the binodal curve of the transverse plait, which can then be realised over its full width, and at still higher temperature it has no longer any points in common with this binodal curve.

If figure 47 of Contribution XV (These Proc. XI p. 904) is compared with the result of this discussion, we see that the temperature of the point C of figure 47 is T_{sp}, and that of the point D the temperature at which the pair of heterogeneous plaitpoints P_2 and P_3 coincide. Already in contribution XV I remarked about fig. 47 that the righthand branch between E and F may be omitted. Then, however the point E must be thought to lie at $p = \infty$, and the point F at $T = 0$. Since then I have not been confirmed in the opinion that this branch should be omitted.

In fig. 47, however, a mistake has slipped in, with regard to the closed curve which represents the concentration of the two liquid phases of the three phase equilibrium; it will certainly not have its highest point in C. My attention was drawn to this circumstance by KOHNSTAMM immediately after the appearance of contribution XV. And this same error is expressed in words on p. 900, where it says that the point C lies on the binodal curve of the equilibrium liquid-vapour, and that $\frac{dp}{dx}$ and $\frac{d^2p}{dx^2}$ are equal to zero in the point C. So these two sentences ought to be omitted, and when KUENEN does not mean anything by his remark but this, I entirely agree with him. But I read more in his remark, and this is the reason why I think I should make these observations. It namely seems to me that KUENEN l.c. means that the double point of the spinodal curve (which is naturally always also a double point of the binodal curve) would always have to lie *outside* the binodal curve of the transverse plait. This will, indeed, be probably possible; then the point where the plaitpoint line $ECDFK$ intersects the line of the three phase equilibria, must lie between C and D of the fig. 47 of contribution XV. Only by way of exception it could have risen as high as the point D. Compare also these Proc. VIII p. 184, where I still harboured some doubt, but finally arrived at the conclusion that I had to locate the intersection of the plaitpoint line with the binodal line before D.

But at least as often, if not oftener, the case will occur that the double point lies *inside* the binodal curve of the transverse plait; in this case the endpoint of the three-phase pressure lies on the branch CE of the plaitpoint line. The foregoing remark may also be expressed thus. KORTEWEG's theorem that the coincidence of two heterogeneous plaitpoints must always take place inside the binodal curve, is interpreted by KUENEN thus, as it seems to me: "The coincidence of two homogeneous plaitpoints must not take place inside the binodal curve." This would mean in fig. 47: "As the point where the plaitpoint line enters the binodal curve, cannot lie on the right of D, it cannot lie on the left of C either". This would have certainly called for a proof, for these two theorems are certainly not identical.

Or if I had to comprise my defense against the objection in one phrase, it would run: When a theorem is true, it does not follow that the reverse of this theorem is true. KORTEWEG's theorem is true and can be considered as self-evident, namely, if we understand by binodal line a line which can be realized. But it does not follow from this that every double plaitpoint inside the binodal curve is a *heterogeneous* double plaitpoint.

Besides I have nowhere asserted that the binodal curve could be entirely realised at T_{sp}. This is only the case at higher temperature. At T below T_{sp} there is connection between the unstable part of the transverse plait and of the longitudinal plait. So the liquid branch of the binodal curve of the transverse plait has a metastable and an unstable part. This is also the case at T_{sp}. Not until higher temperature, i. e. when the plaitpoint of the longitudinal plait lies on the binodal curve of the transverse plait, this binodal curve is entirely to be realised. But KUENEN's objection makes me doubt whether I have expressed my meaning clearly enough.

A simple proof for the theorem that $\left(\frac{d^2v}{dx^2}\right)_{pT}=0$ at the double point, is furnished when the spinodal curve is represented by the aid of the ζ function by:

$$\left(\frac{d^2\zeta}{dx^2}\right)_{pT}=0.$$

The differential quotient is then:

$$\left(\frac{d^3\zeta}{dx^3}\right)_{pT}+\left(\frac{d^3\zeta}{dp^2dp}\right)_{pT}\frac{dp}{dx}=0$$

In case of splitting up both $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}$ and $\left(\frac{d^3\zeta}{dx^3dp}\right)_{pT}$ is equal to zero, and then $\frac{dp}{dx}$ cannot be determined from this equation, but must be found from a quadratic equation. Now $\left(\frac{d\zeta}{dp}\right)_{xT}=v$, and at a double point the two relations $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}=0$, i. e. the condition of a plaitpoint, and $\left(\frac{d^2v}{dx^2}\right)_{pT}=0$ hold. At an ordinary plaitpoint $\left(\frac{d^2v}{dx^2}\right)_{pT}$ is not equal to 0, but then $\frac{dp}{dx}=0$.

My conclusion is this. At the temperatures at which the splitting up takes place the double point can lie inside the joint realizable binodal curves of the longitudinal plait and the transverse plait. That this is impossible has never been proved as yet, and is not to be proved in my opinion.

Above T_{sp} the lefthand and the righthand convex-convex part of the surface that lies within the binodal curve, have united.