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Physics. — “Some remarks on the direction of the binodal curves in the v - x -diagram in a three-phase-equilibrium.” By Prof. J. P. KUENEN.

Professor SCHREINEMAKERS has privately communicated to me the following rule which he has derived from the general theory of plaits and which occurs in a joint paper about to be published by him and Professor D. J. KORTEWEG:

In a three-phase-equilibrium the two binodal curves which pass through an angle of the three-phase-triangle lie either both inside or both outside the triangle.

For the special case of the ψ -surface for binary mixtures this rule may be proved as follows. Choose one of the angles, say 1, and start from the condition where the phases 2 and 3 coincide, a condition which we may always imagine, even though it may not be physically realisable: at this moment the two binodal curves through 1 form one continuous curve. If now 2 and 3 separate the two curves meet at an angle and obviously in the beginning they both lie outside the triangle. As the surface continues to change one of the binodal curves (say the one of the equilibrium 1,2) may pass into the triangle by its direction at a definite moment coinciding with the side 1—3 of the triangle. But it may be shown that at the same moment the second binodal curve coincides with the side 1—2, in consequence of which this curve also passes into the triangle.

The equation which expresses the special position referred to of the binodal curve 1,2 is as follows¹⁾:

$$\left(\frac{dv}{dx}\right)_{12} = \frac{(v_2 - v_1) \frac{\partial^2 \psi}{\partial x \partial v} + (x_2 - x_1) \frac{\partial^2 \psi}{\partial x^2}}{(v_2 - v_1) \frac{\partial^2 \psi}{\partial v^2} + (x_2 - x_1) \frac{\partial^2 \psi}{\partial x \partial v}} = \frac{v_2 - v_1}{x_2 - x_1}$$

Solving for $\frac{v_2 - v_1}{x_2 - x_1}$ we find:

$$\frac{v_2 - v_1}{x_2 - x_1} = \frac{(v_3 - v_1) \frac{\partial^2 \psi}{\partial x \partial v} + (x_3 - x_1) \frac{\partial^2 \psi}{\partial x^2}}{(v_3 - v_1) \frac{\partial^2 \psi}{\partial v^2} + (x_3 - x_1) \frac{\partial^2 \psi}{\partial x \partial v}} = \left(\frac{dv}{dx}\right)_{13}$$

in other words the curve 1,3 coincides with the side 1—2, q. e. d.

Looking through the literature concerning the ψ -surface one finds that in the diagrams the above rule has been often sinned against.

¹⁾ All the differential coefficients without an index refer to the point 1.

Keeping this rule in view and considering the diagram in the neighbourhood of a critical point for two of the phases, where a plaitpoint makes its appearance (or disappears) we at once arrive at the following important law :

When a plait touches a second plait in its plaitpoint the curvatures of the two are of the same sign.

An independent proof of this law may be given using the properties of the curves of constant pressure, the isopiëstics. It is well known that the isopiëstic which touches a plait in its plaitpoint is curved in the same direction as the plait. At the point under consideration the three curves (viz. the binodal with the plaitpoint, the second binodal and the isopiëstic) touch each other. But the isopiëstic cannot touch the second binodal curve simply on the outside, for that would mean, that the point was also one of maximum vapour pressure on the second plait, and it is well known that this is not the case. The isopiëstic and binodal curves must therefore intersect as well as touch, i. e. they have the same curvature, from which it follows that the second binodal is like the isopiëstic curved in the same direction as the plait which it touches.

Analytically the law is expressed by the equality of the two expressions $\left(\frac{d^2v}{dx^2}\right)_{bin}$ and $\left(\frac{d^2v}{dx^2}\right)_p$ which may be easily confirmed by calculation. I find that some time ago a proof of this relation was given by VAN DER WAALS¹⁾, but I must add at once that I do not agree with the view expressed by him that the value of these coefficients should be zero at the point in question, in which case the two curves would have a point of inflexion there.

The condition $\frac{d^2v}{dx^2_p} = 0$ holds at a point where a plait separates into two parts with a plaitpoint on each. VAN DER WAALS assumes a separation of that kind, but it occurs inside the second binodal curve, not on it²⁾, and the condition does not hold at the point where one binodal curve with a plaitpoint emerges from a second binodal curve. If I am right some of the diagrams in VAN DER WAALS' paper would need modification.

The literature on the subject shows again a number of diagrams which are not in harmony with the law enunciated concerning the curvature of the two plaits. The figures in my own treatise on

¹⁾ J. D. VAN DER WAALS. Proceedings XI. p. 900, 1909.

²⁾ Comp. the paper on plaits by KORTEWEG (Arch. Néerl. 24), and e. g. VAN DER WAALS, Proc. X p. 141. 1907.

mixtures ¹⁾ will be found to be correct in this respect: in drawing those I was guided partly by experimental results partly by another law ²⁾ which was deduced from the theory and which comes to this, that the separated two-liquid plait lies outside the vapour-liquid plait, if the two components, as liquids, mix with expansion and vice versa. It stands to reason that this law and the new one must essentially be one and the same.

As regards the direction of the two binodals which meet in an angle of the triangle it was mentioned that they always form an angle and naturally such that the curves enter the metastable part of the surface. A proof of this may be given without directly using the theory of plaits by means of VAN DER WAALS'S formulae. If the two directions coincided at any moment we should have:

$$\begin{aligned} \left(\frac{dv}{dx}\right)_{12} &= \left(\frac{dv}{dx}\right)_{13} = -\frac{(v_2-v_1)\frac{\partial^2\psi}{\partial x\partial v} + (x_2-x_1)\frac{\partial^2\psi}{\partial x^2}}{(v_2-v_1)\frac{\partial^2\psi}{\partial v^2} + (x_2-x_1)\frac{\partial^2\psi}{\partial x\partial v}} = \\ &= -\frac{(v_2-v_1)\frac{\partial^2\psi}{\partial x\partial v} + (x_2-x_1)\frac{\partial^2\psi}{\partial x^2}}{(v_2-v_1)\frac{\partial^2\psi}{\partial v^2} + (x_2-x_1)\frac{\partial^2\psi}{\partial x\partial v}} = -\frac{\left(\frac{v_2-v_1}{x_2-x_1} - \frac{v_3-v_1}{x_3-x_1}\right)\frac{\partial^2\psi}{\partial x\partial v}}{\left(\frac{v_2-v_1}{x_2-x_1} - \frac{v_3-v_1}{x_3-x_1}\right)\frac{\partial^2\psi}{\partial v^2}} = \\ &= -\frac{\left(\frac{x_2-x_1}{v_2-v_1} - \frac{x_3-x_1}{v_3-v_1}\right)\frac{\partial^2\psi}{\partial x^2}}{\left(\frac{x_2-x_1}{v_2-v_1} - \frac{x_3-x_1}{v_3-v_1}\right)\frac{\partial^2\psi}{\partial x\partial v}} \end{aligned}$$

If the common factors in numerator and denominator are not equal to zero we may divide by them and we obtain the condition for a plaitpoint at 1, a case which we may exclude. If the factors are zero the three phases are in a straight line: this has a practical meaning only, if 2 and 3 coincide and we already know that the two binodals at 1 form one continuous curve in that case. Under other circumstances therefore the curves must meet at angle, q. e. d. For the special case that the point 1 lies at the extreme limit of the plait, in the so-called critical end point, the proposition was proved and used by VAN DER WAALS. ³⁾

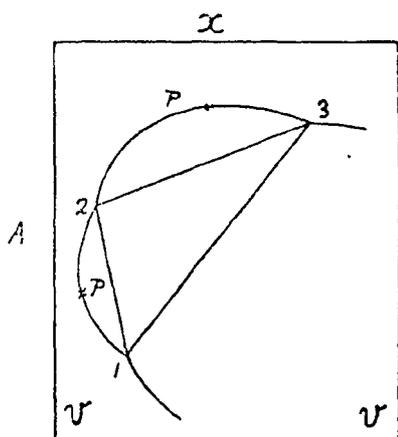
In conclusion it may be pointed out that by taking into account the last proposition one may easily deduce from the $v-x$ diagram

¹⁾ J. P. KUENEN. Theorie u. s. w. von Gemischen, Barth. Leipzig p. 153. et seq. 1906.

²⁾ l. c. p. 158, 159

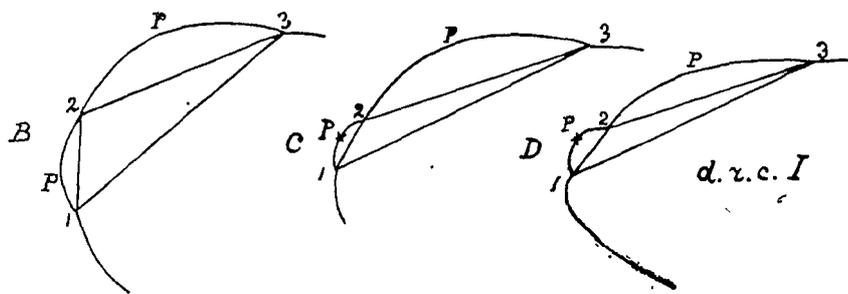
³⁾ J. D. VAN DER WAALS. Proc. XI p. 822. 1909.

the phenomenon of *double retrograde condensation* predicted by VAN DER WAALS by a different method¹⁾. The phenomenon occurs when the vapour is about to form a critical point with one of the liquids while its representative point is still on the vapour side of the plait, (which involves that it has to turn the corner of the plait) and this condition is certainly fulfilled, as VAN DER WAALS pointed out, if there are two liquid layers below the critical temperature of the lower component and this is nearly always the case. But the phenomenon is not limited as might be supposed from his paper²⁾



to the case that the three phase pressure is lower than the vapour pressure of the lower component. In order to show this I will consider the case not discussed by VAN DER WAALS where the three phase pressure is above the vapour pressure of both substances, as with ether and water (Fig. A). The vapour 1 must come together with the liquid 2: therefore either 1 must move round the extreme point of the plait towards 2 or 2 comes

round to 1. In the first supposition (Fig. BCD) the maximum in the vapour pressure which lies hidden inside the triangle appears outside, at the moment when 1 and 2 have the same composition $x(B)$,



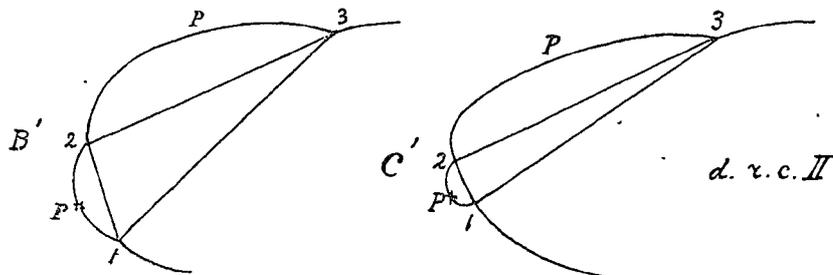
gradually moves off the plait and disappears; at this moment the plaitpoint P belonging to the equilibrium 1,2 passes over to the liquid side, and the case has now become identical with that considered

¹⁾ l. c. p 816, sqq.

²⁾ PH. KOHNSTAMM and J. CHR. REEDERS. Proc. XI p. 917. 1909. Professor KOHNSTAMM draws my attention to a note in a recent paper by the same authors in the September Meeting (p. 272) where the limitation is withdrawn.

by VAN DER WAALS. The necessity of double retrograde condensation (fourfold intersection with a line // v -axis) is seen in figure D .

In the second supposition (Figs. $B'C'$) 2 passes through the critical end point (B') and immediately after we again obtain the configuration which involves double retrograde condensation with this peculiarity



however, that the first retrograde condensation which occurs on compression is retrograde condensation "of the second kind" owing to the position of the plaitpoint on the vapour side. The phenomenon as a whole might therefore be called *double retrograde condensation of the second kind*. The maximum vapour pressure disappears inside the triangle itself in consequence of the transformations which we know from KORTWEG'S investigations take place inside the plait in this case. Whether the first or the second supposition is the correct one, say for ether and water, I shall not try to decide.

Mathematics. — "*The characteristic numbers of the prismotope.*"

By Prof. P. H. SCHOUTE.

1. *Mode of generation.* Let $S_{n_1}, S_{n_2}, \dots, S_{n_p}$ represent a certain number p of spaces respectively of n_1, n_2, \dots, n_p dimensions having by two no point in common but the point O common to them all. Let us assume in each of these spaces a definite polytope with O as one of its vertices, and let us denote the polytope in S_{n_1} by $(P)_{n_1}$, that in S_{n_2} by $(P)_{n_2}, \dots$, that in S_{n_p} by $(P)_{n_p}$. Now let us move $(P)_{n_2}$, remaining equipollent to itself, in such a way that the point coinciding originally with O coincides successively with each point within $(P)_{n_1}$; then the locus of all the positions of $(P)_{n_2}$ is a prismotope with two constituents $(P)_{n_1}, (P)_{n_2}$ which may be represented by the symbol $(P)_{n_1}; (P)_{n_2}$. Now let us move $(P)_{n_3}$, remaining equipollent to itself, in such a way that the point coinciding originally with O coincides successively with each point within $(P)_{n_1}; (P)_{n_2}$; then the locus of all the positions of $(P)_{n_3}$ is a prismotope with three