Physics. — "*On the Occurrence of Solid Substance in Binary Mixtures with Unmixing*" I. By Prof. F. E. C. SCHEFFER. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of November 30 1918).

1. *Introduction.* When two phases coexist in a binary system, the condition that the temperature and the three quantities $\left(\frac{d\psi}{dv}\right)_{xT}$, $\left(\frac{d\psi}{dx}\right)_{vT}$, and $\psi - v\left(\frac{d\psi}{dv}\right)_{xT} - x\left(\frac{d\psi}{dx}\right)_{vT}$ shall be equal for the two phases, must be satisfied. On the surface $\psi = f(v, x)$, constructed for a definite temperature, the coexisting phases are obtained by rolling a bi-tangent plane over this surface. Another method to find the coexisting phases consists in this that the system of curves $\left(\frac{d\psi}{dv}\right)_{xT} =$ = constant (p-lines), $\left(\frac{d\psi}{dx}\right)_{vT}$ = constant (q-lines) and $\psi - v\left(\frac{d\psi}{dv}\right)_{xT} - x\left(\frac{d\psi}{dx}\right)_{vT}$ = constant (potential lines) are thought to be traced projected on the v—x plane; then two points on the ψ-surface indicate coexisting phases when through the projections of these points run a same p-line, a same q-line, and a same potential line.

The points indicating coexisting phases, furnish in the v—x-projection a locus the inclination of which is determined by:

$$\left(\frac{dv_1}{dx_1}\right)_{bin} = -\frac{(v_2 - v_1)\dfrac{d^2\psi}{dv_1 dx_1} + (x_2 - x_1)\dfrac{d^2\psi}{dx_1^2}}{(v_2 - v_1)\dfrac{d^2\psi}{dv_1^2} + (x_2 - x_1)\dfrac{d^2\psi}{dv_1 dx_1}}, \quad . \quad . \quad . \quad (1)$$

in which the indices 1 and 2 refer to the two coexisting phases [1]).

The indicatrix in a point of the ψ-plane is given in first approximation by the equation:

$$v^2\frac{d^2\psi}{dv_1^2} + 2vx\frac{d^2\psi}{dv_1 dx_1} + x^2\frac{d^2\psi}{dx_1^2} + \alpha v + \beta x + \gamma = 0 \quad . \quad . \quad (2)$$

[1]) VAN DER WAALS—KOHNSTAMM. Thermodynamik. II. S. 196, equation 1.

When equation (1) is written in the form:

$$\left(\frac{dv_1}{dx_1}\right)_{bin}\frac{v_2-v_1}{x_2-x_1}\frac{d^2\psi}{dv_1^{\,2}}+\left[\left(\frac{dv_1}{dx_1}\right)_{bin}+\frac{v_2-v_1}{x_2-x_1}\right]\frac{d^2\psi}{dv_1 x_1}+\frac{d^2\psi}{dx_1^{\,2}}=0,. \qquad (3)$$

it appears from (2) and (3) that the binodal line and the nodal line represent conjugate diameters in the indicatrix, which has been demonstrated by KORTEWEG [1]).

2. *The Relative Situation of Binodal Lines and Nodal Lines.*

A great number of inferences which are of importance for the treatment of the more intricate cases of heterogeneous equilibrium, which may present themselves for binary mixtures, may be made from the above mentioned conclusions from the theory of binary mixtures, which have been known already for a long time.

We shall imagine *two* binodal lines going through a point of the ψ-plane; each binodal line with the nodal line belonging to it is a set of conjugate diameters in the indicatrix. Depending on the form of the indicatrix we now get the following cases:

a. $\dfrac{d^2\psi}{dv^2}\cdot\dfrac{d^2\psi}{dx^2}>\left(\dfrac{d^2\psi}{dv\,dx}\right)^2$. *Elliptical point.*

From the well-known thesis of the ellipse that two pairs of conjugate diameters separate each other, follows when we indicate the direction of the tangents to the binodal lines, by b_1 and b_2, that of the nodal lines by n_1 and n_2:

Moving in a definite direction round the elliptical point, the succession of binodal and nodal lines is:

$$b_1\ b_2\ n_1\ n_2.$$

Now the two phases coexisting with A (fig. 1) can:

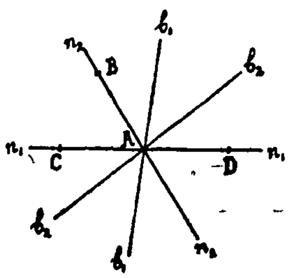

Fig. 1.

1. form a three-phase triangle ABC, so that the two binodal lines lie entirely outside the triangle, and

2. form a three-phase triangle ABD, so that the two binodal lines lie on one side of A within the triangle.

As, however, binodal lines within the triangle indicate two-phase coexistences which are metastable with regard to the third phase (the three phase equilibrium is, namely, stable inside the three-phase triangle [2]), it appears that the above mentioned conclusion can also be expressed in the following words:

[1]) KORTEWEG. Arch. Néerl. 24, 57 and 295 (1891).

[2]) We assume that there occur no points on the ψ-surface where the surface seen from below is concave-concave.

When one of the phases participating in the three-phase equilibrium corresponds with an elliptic point on the ψ-surface, the prolongations of the (stable) binodal lines lie either both inside or both outside the three-phase triangle.

b. $\dfrac{d^2\psi}{dv^2}\cdot\dfrac{d^2\psi}{dx^2}=\left(\dfrac{d^2\psi}{dv.dx}\right)^2$. *Parabolical point.*

From equation (1), which can easily be transformed into:

$$\left(\frac{dv_1}{dx_1}\right)_{bin}=-\frac{(v_2-v_1)+(x_2-x_1)\dfrac{\dfrac{d^2\psi}{dx_1^2}}{\dfrac{d^2\psi}{dv_1dx_1}}\;\dfrac{d^2\psi}{dv_1dx_1}}{\dfrac{d^2\psi}{dv_1dx_1}\;(v_2-v_1)+(x_2-x_1)\dfrac{\dfrac{d^2\psi}{dv_1dx_1}}{\dfrac{d^2\psi}{dv_1^2}}\;\dfrac{d^2\psi}{dv_1^2}} \quad . \quad . \quad . \quad (4)$$

and from $\left(\dfrac{d\psi}{dv}\right)_x=-p=$ constant and $\left(\dfrac{d\psi}{dx}\right)_v=q=$ constant, for which the following relations are valid:

$$\left(\frac{dv_1}{dx_1}\right)_p=-\frac{\dfrac{d_2\psi}{dv_1dx_1}}{\dfrac{d^2\psi}{dv_1^2}} \text{ and } \left(\frac{dv_1}{dx_1}\right)_q=-\frac{\dfrac{d^2\psi}{dx_1^2}}{\dfrac{d^2\psi}{dv_1dx_1}},$$

follows that equation (4) for a parabolic point reduces to:

$$\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_p=\left(\frac{dv}{dx}\right)_q.$$

Hence the two binodal lines touch the p- and the q-lines, and accordingly they are in contact with each other; the two nodal lines form arbitrary angles with the binodal lines and also with each other.

When one of the phases participating in the three-phase equilibrium corresponds with a parabolic point on the ψ-surface, there is contact between the two binodal lines; the binodal lines either lie partly inside or entirely outside the three-phase triangle.

c. $\dfrac{d^2\psi}{dv^2}\cdot\dfrac{d^2\psi}{dx^2}<\left(\dfrac{d^2\psi}{dvdx}\right)^2$. *Hyperbolical point.*

In a hyperbola pairs of conjugate diameters do not separate each other. Hence:

Moving in a definite direction round a hyperbolical point, the order of binodal lines and nodal lines is:

$$b_1\, b_2\, n_2\, n_1 \text{ or } b_1\, n_2\, b_2\, n_1\,.$$

54

When the triangle in fig. $2a$ (order $b_1\, b_2\, n_2\, n_1$) is represented by ABC, the two binodal lines lie entirely outside the triangle, when by ABD, they lie both partly inside it, whereas in fig. $2b$ (order $b_1\, n_2\, b_2\, n_1$) one binodal line lies partly inside, one entirely outside the triangle both for the three-phase equilibrium ABC and for ABD.

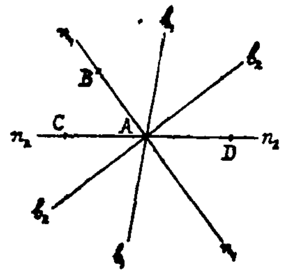

Fig. $2a$.

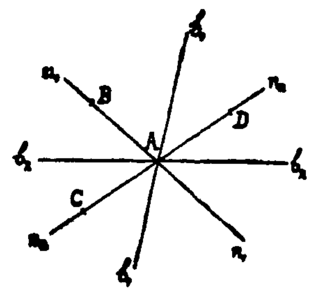

Fig. $2b$.

3. Of the conclusions discussed in § 2 the last of those mentioned under a is not new. Some years ago KUENEN proved this thesis by another method [1]). I think I have demonstrated in what precedes that the relative situation of nodal lines and binodal lines can directly be derived in a general way from the already long known properties of the ψ-surface [2]).

Though the realizable parts of the ψ-surface are only indicated by elliptical points, the general discussion of § 2 has the advantage that it points out a regularity for the whole ψ-surface. The above discussed conclusions are of great importance when we want to examine the possible coexistences of solid by the side of fluid. By the aid of the rules discussed in § 2 it is possible to indicate the relative situation of the binodal lines solid-fluid and fluid-fluid in every point. They are almost indispensable in this study, because when these rules are not observed, we are often in danger in the more intricate cases of mistaking impossible cases, for possible ones, especially in the metastable and unstable region. And for a complete survey of these existences the not realizable parts of the ψ-surface cannot be dispensed with.

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1) KUENEN. These Proceedings. XIV p. 420.

2) *Note added during the correction of the Dutch proofs*. The theses of § 2 are not only valid for the ψ-surface, but for any surface, hence also for the ζ-surface. In BAKHUIS ROOZEBOOM's Heterogene Gleichgewichte III. 2. SCHREINEMAKERS thus discusses analogous rules (p. 115 et seq.); the situations in the metastable region have, however, been only partly treated (p 340 et seq.).

4. *Coexistence of Solid by the Side of Fluid Phases.*

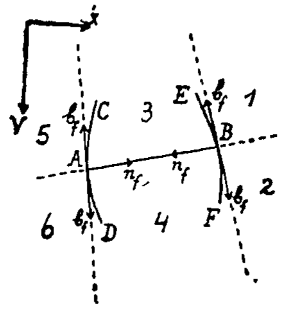

Fig. 3.

When the curves CD and EF in fig. 3 represent projections of binodal lines of a plait on the ψ-surface, the v—x-plane is divided into six regions by the nodal-lines AB and the tangents to the binodal lines in A and B. When also a solid phase S coexists with A and B, the point representing the solid phase can lie in each of these regions. Then the rules of § 2 easily give the course of the binodal line through A and B for fluid phases existing by the side of solid for each of these cases. When the solid substance is the second component, the most frequently occurring situations are those of the regions 2 and 1. The first case is represented in fig. 4a, the second in fig. 5a; the plait has been assumed to be stable for both, i. e. to lie on the convex-convex part of the ψ-surface (seen from below).

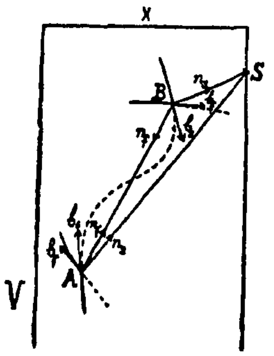

Fig. 4a.

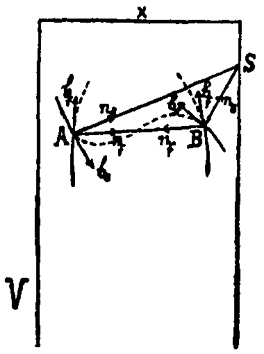

Fig. 5a.

The points A and B are, therefore, elliptical, and the rules of § 2a determine the situation of the binodal line for fluid phases coexisting with solid in the two points, as it has been indicated in figs. 4a and 5a. These situations correspond to the P-x-figures indicated in figs. 4b and 5b, in which the three-phase coexistence is again indi-

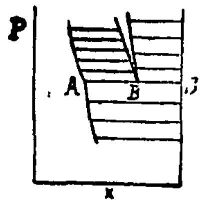

Fig. 4b.

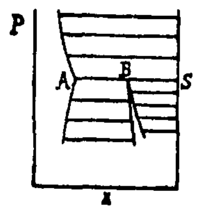

Fig. 5b.

cated by ABS, and the two-phase regions are hatched; the hatching-lines indicate nodal lines.

The transition case which causes fig. $4a$ to pass into fig. $5a$ now also often occurs for the practically occurring heterogeneous equilibria. (An instance of this is discussed in § 6). When namely the point S lies on the prolongation of the line AB, the nodal lines n_s and n_f coincide (n_s is the nodal line drawn from a fluid to the solid phase, n_f to the other fluid phase). The theorem of § $2a$ then requires that also b_s and b_f coincide, in other words that the two binodal lines are in contact.

When a solid phase lies on a nodal line of the fluids, the binodal lines fluid-fluid and fluid-solid touch each other in the nodes.

In a perfectly analogous way it also follows that:

If the nodal line solid-fluid touches the binodal line fluid-fluid, the binodal line solid-fluid touches the nodal line of the fluid phases.

All the cases that can occur for a stable plait, have now been discussed. It, however, repeatedly occurs that part of the plait indicates unstable states; in the points of the binodal lines which are situated within the spinodal line the surface is namely convex-concave, and the points themselves are hyperbolical. In analogy with figs. $4a$ and $5a$ we can now again construct two figures, which are applicable when one of the binodal lines consists of hyperbolical points. (The case, that both binodal lines consist of hyperbolical points is not considered; the discussion is self-evidently just as simple). In these cases we get figs. 6 and 7. In both point A is

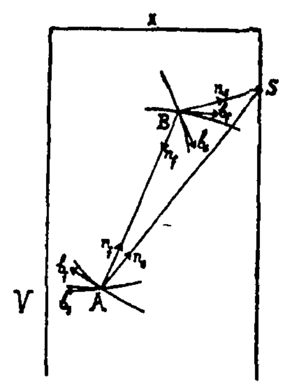

Fig. 6.

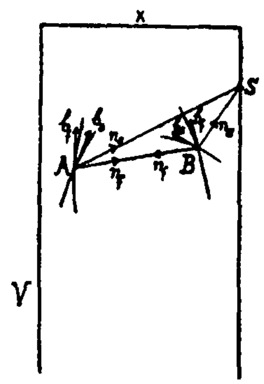

Fig. 7.

given as hyperbolical, point B as elliptical point. The corresponding P-x-diagrams are easy to construct; they have, therefore, been omitted; besides the coexistences are not realizable, and are accordingly devoid of practical importance.

5. *The Four-Phase Equilibria.*

When on the ψ-surface simultaneous coexistence with solid occurs for a three-phase equilibrium of fluid phases, the number of nodal lines and binodal lines passing through the nodes, amounts to three. When we assume that the three-phase coexistence takes place on the stable part of the ψ-surface, the three fluid phases participating in this equilibrium are indicated by elliptical points; the relative situation of the three pairs of conjugate diameters is again determined by *the rules of § 2a in this sense that these theorems hold* good for every combination in sets of two of the 3 pairs of conjugate diameters.

6. *Applications.*

In a treatise on the phenyl- and tolylcarbaminic acids recently published in these Proceedings it was pointed out that the different P-T-figures which are found for these homologous compounds, can be derived from each other by moving the quadruple point along the three-phase line L_1L_2G[1]). When the quadruple point reaches the critical endpoint, it is still just stable; this is the transition case, which connects this type of binary systems with the type sulphuretted hydrogen-ammoniac, where the coexistence L_1L_2G does not appear stable any more.

Such a transition is also found for binary systems without compound, a fact which BÜCHNER[2]) already pointed out in his Thesis for the Doctorate. We then get a transition from a system with a quadruple point to the type diphenylamine-carbonic acid. The transition itself has not been studied by BÜCHNER; as it is, however, possible that by a suitable choice of the components we can get close to this transition case — in the cited paper I drew attention to the system as-o-xylidine-carbonic acid — the study of this transition case has probably not only theoretical importance.

This transition can now be simply followed by the aid of the rules mentioned in §§ 1—5; it has, indeed, been the study of this transition that induced me to seek the regularities mentioned in what precedes.

A complete discussion of this transformation is not possible with the aid of the above rules alone. For these only indicate the course of binodal and nodal lines in the neighbourhood of the nodes. Yet this is already sufficient to give us an insight into the phenomena that will make their appearance in this transition case.

For this purpose I will imagine the ψ-surface to be constructed for the temperature of the critical endpoint ($L_1 = G$). We may then expect a situation as indicated by fig. $8a$ or $8b$. The plaitpoint P_1

1) These Proceedings. 21. 664. (1919).
2) BÜCHNER. Thesis for the Doctorate. Amsterdam 1905.

represents L_1 and L_2 becoming identical, P_2 represents L_1 and G

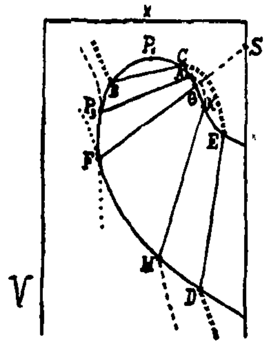

Fig. 8*a*.

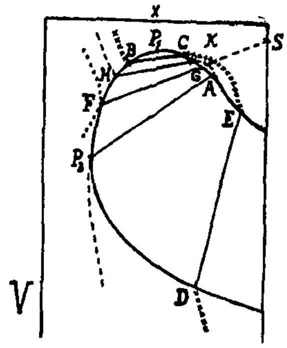

Fig. 8*b*.

becoming identical; the plait of P_2 has disappeared in this last point within the longitudinal plait; it has been omitted for the sake of the lucidity of the figures. The liquid coexisting with the fluid phase P_2 is indicated by A. The nodal lines BC in the plait P_2P_1A present a situation corresponding to fig. 5*a*, the nodal lines DE to fig. 4*a*. It follows from this that a nodal line may be drawn between BC and DE, the prolongation of which passes through S (FG in the figs. 8*a* and 8*b*). Hence in the points F and G a possibly occurring binodal line for fluid phases coexisting with solid touches the binodal line fluid-fluid. (See § 4). In fig. 8*a* the nodal line FG lies below P_2A, in fig. 8*b* it lies above it.

When we now inquire into the course of the binodal line solid-fluid, all the possible situations can be easily surveyed by rolling a tangent plane for continually decreasing values of ψ_s over the surface. When the ψ-value of S is chosen high, the tangent curve will only intersect the plait on the righthand of DE; with lower value of ψ_s a curve will make its appearance which also passes through P_1; further the curve will intersect the plait both in the neighbourhood of P_1 and in the neighbourhood of DE. Such a situation is represented by the curve indicated by crosses. When ψ_s is made to shift further, we get a curve passing through P_2 indicated by a line of dashes. Finally the tangent curve will move in such a way that the two points of intersection on the two binodal branches approach each other, and at the coincidence in F and G contact of the two binodal curves takes place; the curve for solid-fluid lies in F outside the binodal line fluid-fluid and is stable; for G it lies, however, in the covered region. By the aid of the rules of § 2 it may be derived that the traced situations are the correct ones. It should, however, be pointed out that according to these rules the binodal lines in P_2 touch and intersect.

The three binodal lines for solid-fluid indicated in the two figures correspond to the equilibria marked by the same letters in figs. 9*a* and *b*. It will be clear from what has been discussed that the point

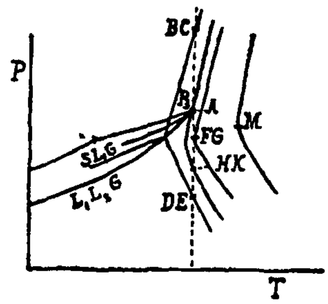

Fig. 9*a*.

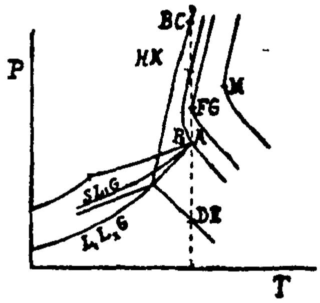

Fig. 9*b*.

where $\frac{dP}{dT} = \infty$, may lie both at higher and at lower pressure than P_2 [1]). This point corresponds to a nodal line (FG) passing through S in figs 8*a* and 8*b*. On still further displacement the binodal curve for solid lies outside the longitudinal plait. Then the point of contact can appear at higher temperature; in figs, 9*a* and *b* such a point of contact is indicated by M. The situation of the three-phase line passing through M has been found experimentally by BÜCHNER in the system diphenylamine-carbonic acid [2]), by ADA PRINS in the system ethane-naphtalene [3]).

7. The transition of the systems with quadruple point SL_1 L_2G to the type diphenylamine-carbonic acid has been derived in the preceding paragraph by the aid of the rules given in § 2. The shape of the binodal curves is indicated by them, however, only in the neighbourhood of the points of intersection. The course throughout the region, which is remarkable especially in the covered region, could be dispensed with in the above discussion. A full insight can only be obtained by considerations on the course of binodal lines solid-fluid in general. For this the discussion of some loci on the ψ-surface is required.

(*To be continued.*)

November 20th 1918. *Delft. Technical Highschool.*

[1]) At lower temperatures this point lies in the covered region; it will appear on a fuller treatment of the transformation that the displacement of this point follows easily from the transition of the two three phase lines SL_1L_2 and SL_2G into each other (unstable ridge), and the change in this on approach to the critical endpoint. These changes may also be directly examined by the aid of the rules of § 2.

[2]) BÜCHNER. Thesis for the Doctorate. Amsterdam. 1905, p 85, fig. 36.

[3]) ADA PRINS. These Proc. XVII p. 1095.