Citation:

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Chemistry. — *"On the continuous connection between the three-phase lines which indicate the equilibria between the two components in the solid condition with liquid and vapour respectively, in a binary system."* By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

In consequence of the theoretical essay of Prof. VAN DER WAALS on the equilibrium between a solid substance and a fluid phase, particularly in the neighbourhood of the critical condition [1]) SMITS studied in 1905 the hidden equilibria in the P-x-sections of BAKHUIS ROOZEBOOM's spacial figure below the eutectic point [2]). The two lines for the fluid phases which coexist with solid A and solid B, respectively, intersect each other in the isothermic sections below the eutectic point at two three-phase pressures: $S_A\,S_B\,L$ and $S_A\,S_B\,G$ which indicate stable conditions for the case that $\frac{dp}{dt}$ of the solid-liquid line of the components is negative, which was supposed to be so in the above mentioned paper.

As a further study as to the course of the lines S_A-Fluid and S_B-Fluid can enlighten us as to the continuous connection of the two said three-phase lines in the spacial figure I will trace its position for the most simple case: complete miscibility in the liquid condition, separation in the solid condition and gradual fall of the coexistence pressure $L-G$ from the one component to the other.

If for this purpose we consider the condition at a temperature situated a little above the quadruple point, the constant pressure lines will show in the V-x figure a course as indicated in Fig. 1, where the pressure continuously increases along an isometric line from $x=0$ to $x=1$. These isopiests have a vertical tangent on the lines ehf and ilk, the geometrical place where $\frac{d^2\psi}{dv^2}$ on the ψvx plane of the fluid phases is zero.

The points H and G, S and R situated on the binodal line ab and cd indicate the liquid and vapour which under three-phase pressure can coexist with S_A and S_B, respectively.

Let us now imagine that all the ψ values belonging to the $v—x$ points are deposited perpendicularly on the plane of drawing. The tangent plane turning through $\psi_{S_A}(V)$ over the surface of the fluid phases will describe a line $LGEDBAK$ indicating the fluid

1) Proc. 1903 Oct. 31.
2) Proc. 1905 Dec. 30.

phases which may coexist with the first component in the solid condition. In complete analogy herewith, by the moving of the tangent plane through $\psi_{S_B}(W)$, a line $QRPONMSK$ is formed indicating the fluid phases coexisting with S_B; on LG and QR solid A and solid B, respectively, exists with a gasphase; on HK and SK with a liquid phase [1]).

The two lines have each a point of maximum and a point of minimum pressure at the place where they intersect the spinodal line (egf and imk). The fact that in the intersecting points with the spinodal line the isopiest really touches the coexistence line solid-fluid is obvious from the equation deduced by van VAN DER WAALS [2]):

$$\frac{d^2\psi}{dv^2_f} v_{sf} \frac{dp}{dx_f} = (x_s - x_f) \left\{ \frac{d^2\psi}{dx_f^2} \frac{d^2\psi}{dv_f^2} - \left(\frac{d^2\psi}{dx_f dv_f} \right)^2 \right\} .$$

On the spinodal line, the factor of $x_s - x_f$ is zero; as the other quantities in this equation have generally all a finite value $\frac{dp}{dx_f}$ will be 0, which consequently points to the appearance of a maximum or a minimum pressure and which, therefore takes place in the points B and M (minimum) and P and D (maximum).

In the points A, E, N, and O where the nodal line Solid-Fluid touches the isopiest, $v_{sf} = 0$. From the above equation it, therefore, follows that in the said points the value of $\frac{dp}{dx_f}$ is infinite.

If, now, we observe the progressive change of the pressure values on the two coexistence lines S_A-Fluid and S_B-Fluid, and by the aid of this construct the corresponding P-x figure (Fig. 2), the P-x lines will show a vertical tangent in A, N, E, and O ($V_{sf} = 0$), in D, P, B, and M a horizontal tangent (points of the spinodal line) and in the points K, I, and F an intersection (three-phase pressures). From a joint examination of the V-x and the P-x figure it will then appear that the other numerous intersections are only incidental and do not indicate a coexistence of S_A, S_B and one fluid phase, because the intersecting points do not represent *one* but *two* different fluid phases with a different volume.

At the temperature to which Figs. 1 and 2 refer five three-phase pressures may occur: S_ALG, S_BLG and S_AS_BL (stable), S_AS_BG (metastable) and S_AS_BFl labile [3]).

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1) It is assumed here that thesolid substances increase in volume on beiug melted.

2) Cont. II. 13 and l. c.

3) For clearness' sake the fluid phases between the spinodal line have been indicated here by "Fl".

If, now, we observe what changes occur at various temperatures, it will be noticed that ψ_S, which value is situated under the ψ-plane for the fluid phases, falls with elevation of temperature $\left(\frac{d\psi}{dt} = -\eta,\right.$ in which η is taken as positive$\left.\right)$ and as η_G and $\eta_L > \eta_S$, shows a *smaller* fall than the ψ-plane for the same increase of temperature. The points of the solid substance, therefore approach the ψ-plane of the fluid phases; consequently the line described by the tangent plane turning over the surface will shift more towards the side of the solid phase; the line $LGEDBAK$ therefore, shifts towards the left; $QRPONMSK$ towards the right.

The consequence of this shifting will, therefore, be that the points I and F approach each other finally coinciding in a point where the two curves of the fluid phases, coexisting with S_A and S_B, come in contact with each other.

In quite an analogous manner, it will be obvious, that on lowering the temperature the points I and K approach each other and finally coincide also in one point. Before, however, I and K can meet, K will have to arrive within the binodal line and therefore in the metastable region; just at the moment that K passes the binodal line, F will pass from the metastable region into the stable one: this transition takes place in the quadruple point. where the stable coexistence of four phases is possible.

We, therefore, conclude that there exists a temperature traject where three three-phase pressures may occur which is limited at the higher temperature by the coincidence of I and F, at the lower temperature by the coincidence of K and I. The consequence of this will be, that the two three-phase lines $S_A\,S_B\,L$ and $S_A\,S_B\,G$ are continuously connected in their P-T- projection. In order to be able to judge about the shape of this connecting line we will observe a little more closely the transformation at temperatures where I and F approach each other.

When we consider that in D and P (points of the spinodal line) the isopiest touches the coexistence lines Solid-Fluid and that therefore when D and P coincide the two branches must necessarily have a common tangent, it is evident that the two intersecting points must necessarily coincide on the spinodal line. If this is to happen I will have to move through O, and F through E, a necessity which we read at once from the V-x-figure and which accounts for the fact that in the P-x-figure, just before the contact takes place, a situation occurs as indicated in Fig. 3^b. (In the V-x and P-x projection of

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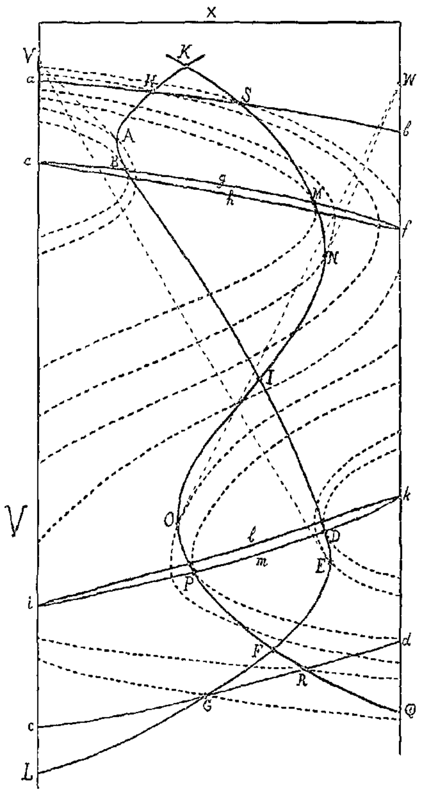

Fig. 1.

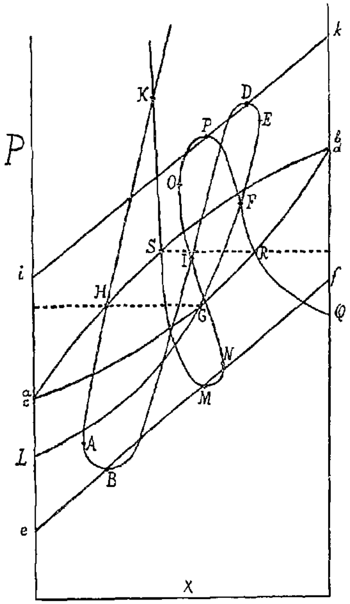

Fig. 2.

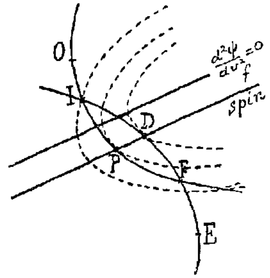

Fig. 3a.

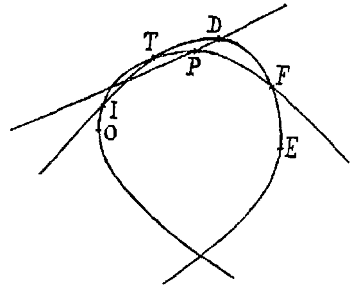

Fig. 3b.

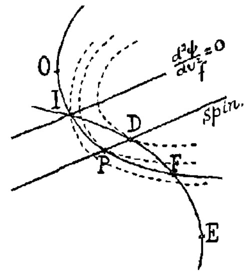

Fig. 4a

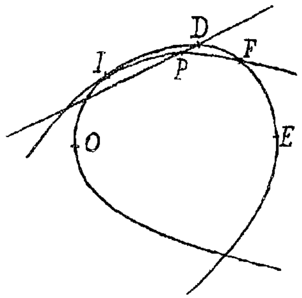

Fig. 4b.

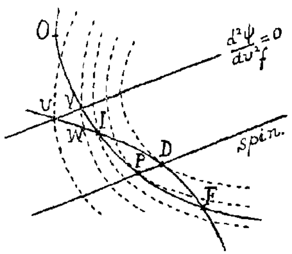

Fig. 5a.

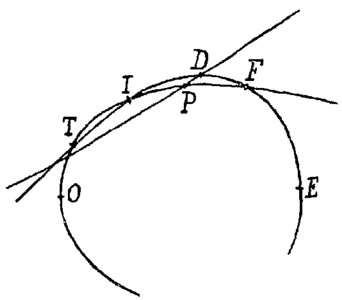

Fig. 5b.

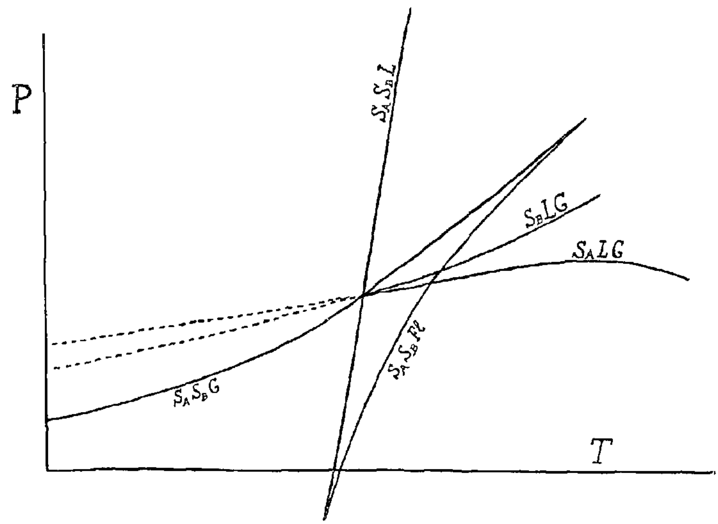

Fig. 6

Fig. 3^a and 3^b the corresponding points are indicated by the same letters). The point T is here a point of incidental intersection; this will be clearly seen by looking at the line $\frac{d^2\psi}{dv^2}=0$, which is indicated in Fig. 3^a. The point where $\frac{d^2\psi}{dv^2}=0$ intersects the line IDF has a higher pressure than the points of equal x of the line IPF, and in the intersecting point of $\frac{d^2\psi}{dv^2}=0$ with the latter, the pressure is higher than in the point of equal x on the line IDF. It will be obvious, that somewhere on IDF there will be found a point where the pressure is equal to that at a point of equal x on IPF; this point is the intersecting point T.

At an elevation of temperature I shifts more and more towards the line $\frac{d^2\psi}{\partial v^2}=0$. When it has reached this line, I and T will so there is a contact in this point have coincided; as indicated in Fig. 4^a and 4^b.

If now, on a further elevation of temperature, the point I arrives between the line $\frac{d^2\psi}{dv^2}=0$ and the spinodal line, the points I and T will have exchanged their places (See Figs. 5^a and 5^b). It will be obvious that the point of incidental intersection T again corresponds here with a point in the figure 5^b of the line OV and UW of equal x and also lying on the same isopiest.

If the temperature is still further increased the points I and will finally coincide in D and P. As now p_I and $p_F < p_P$ and $\frac{dp_P}{dT}$ is always positive (because P moves along the spinodal line towards the side of higher pressure and the pressure in each point rises with an elevation of temperature)[1]) the coincidence of I and F with P will necessarily cause $\frac{dp_I}{dT}$ and $\frac{dp_F}{dT}$ to be positive also.

On the coincidence of I and F, $\frac{dp_I}{dT}$ and $\frac{dp_F}{dT}$ will moreover become equal, because in $\frac{dp}{dT_x}=\frac{W_{sf}}{TV_{sf}}$ the quantities W_{sf} and V_{sf} then relate

[1]) This is also shown from $\frac{dp}{dT_x}=\frac{W_{sf}}{TV_{sf}}$, because V_{sf} in P is negative and W_{sf} also.

to one and the same fluid phase. On continued elevation of temperature only incidental intersections in the P-x projection remain.

In the P-T-projection the three-phase line S_A-S_B-Fluid will, therefore, have always positive values for $\frac{dp}{dT}$ [1]; there exists a temperature traject where the pressure at constant temperature is trivalent; the stable-metastable branch is connected with the labile branch by means of a cusp. The connection is indicated in the P-T-projection of fig. 6.

Physics. — "*The magnetic separation of absorption lines in connection with sun-spot spectra.*" (Third Part) [2]. By Prof. P. ZEEMAN and Dr. B. WINAWER.

Demonstration of oblique position of vibrations by means of half wave-length plate.

34. The observations published in our two preceding communications relate to the region between $\vartheta = 90°$ and $\vartheta = 39°$, the two principal directions inclusive. We now intend to describe in this third, conclusive, part of our paper experiments relative to the remaining region between $\vartheta = 39°$ and $0°$.

This region seemed very interesting because under suitably chosen circumstances it probably would contain the angle ϑ_1 of LORENTZ, separating the regions of the longitudinal and the transverse magnetic effect. The principal object we had in view in undertaking this third part of our investigation was to prove experimentally the existence of an angle of the kind mentioned. We think we attained our purpose.

Before proceeding to describe these experiments, we shall mention a method for verifying the results (24—32) relating to the oblique position of the vibration ellipses of the outer components and that of the vibrations of the inner components, but without commutation of the current in the electromagnet.

Whereas in our former experiments the *difference* of the intensity of the components by *commutation* of the current gives the proof for the obliquity of the components, the half wave-length plate demonstrates it at once.

A half wave-length plate with one of its principal directions situated horizontally and limited by a horizontal line is placed near the source

[1]) A quite analogous view may be applied to the coincidence of I and K.

[2]) Continued from these Proceedings Vol. XIII p. 35, 1910.