

Citation:

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Physics. — “*The P-T-X-spacial figure for a system of two components which are miscible in the solid or liquid crystalline state in all proportions.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

When we project the spacial figure mentioned in the title above it appears that its most remarkable feature is this that three two sheet surfaces must intersect viz. the vapour-liquid sheet, the vapour-mixed-crystal sheet, and the liquid-mixed-crystal sheet, of which we know that for the simplest case, i.e. for the case that these sheets possess neither maximum nor minimum, they show great resemblance in form.

To examine how this intersection takes place we consider first of all a p - x -figure for a temperature below the triplepoint temperature of the two components.

If we call as is usual, the component with the highest vapour tension (and the lowest triple-point temperature) A , this p - x -diagram has a shape as indicated in fig. 1.

On line acb we find the mixed-crystal phases, which coexist with the vapour phases, which lie on the line adb .

Between these two curves lies the region for vapour + mixed-crystal, $G + F$, and above the line acb the region for the mixed-crystals F , and under adb the region of the vapour G . If now we choose a temperature above the triple-point temperature of A , but below that of B , and if we assume for a moment that at the temperature considered A is found in a solid, so supersolidified state, we get a p - x -figure as indicated by $afbga$ in fig. 2, which is quite analogous to that represented in fig. 1.

Solid A , however, being metastable at this temperature, part of this p - x -figure will be metastable on the A -side, and now the question rises what stable equilibria will take the place of these metastable equilibria.

This is immediately seen when we imagine the case, that the two components are liquid at the temperature considered, and so B occurs in superliquefied state.

In this case we should find a p - x -figure as indicated by $cldgc$, where we notice that d lies below b , and c above a , b and c denoting the vapour tension of metastable states of A and B .

The line cld indicates here the liquid phases coexisting with vapour phases on cgg .

The p - x -figure $afbga$ being metastable on the side of A and $cldgc$ being metastable on the side of B , it is at once evident that

the stable p - x -figure will contain the lefthand part of the former and the righthand part of the latter p - x -figure, which parts will meet where a vapour phase coexists at the same time with a liquid phase and with a mixed-crystal phase.

As follows from the diagram the vapour branches of the two p - x -figures intersect in g , so that g is a vapour which does not only coexist with the liquid l , but also with the mixed-crystal phase f .

So the three-phase-equilibrium $G + L + F$, which is non-variant at constant temperature constitutes the transition between the series of mixed-crystal phases af , and the series of liquid phases ld , which can coexist at a series of pressures with vapour phases of different concentration.

We find the region of the liquid L above the line dl and the region of the mixed crystals F above the line af . The two regions are separated by a region of liquid + mixed crystals lying between the lines lq and fq .

If we now draw some p - x -figures corresponding with different temperatures in the same graphical representation beginning with the triple point temperature of A , and ending with the triple-point temperature of B , we get what is represented in fig. 3.

Figure ab corresponds to the triple point temperature of A and a_1b_1 , to that of B , the p - x -figures a_1b_1 and a_2b_2 , referring to intermediate temperatures.

From this collection of p - x -figures we see that when we join the corresponding points of the different three-phase-pressure lines glf , a three-phase-region is formed composed of two two-phase-regions, first of the two-phase-region for the equilibria between vapour and liquid, and secondly of a two-phase-region for the coexistence of liquid and mixed crystals.

If we think the p - x -diagrams corresponding with the different temperatures placed in succession, the vapour-lines form a vapour-sheet, the liquid-lines a liquid-sheet, and the mixed-crystal-lines a mixed-crystal-sheet.

The line bgg_1a_2 indicates the intersection of the vapour-sheet of the mixed-crystals¹⁾ with the vapour-sheet of the liquid phases, the line bl_1a_2 that of the liquid sheet of the mixed-crystals with the liquid sheet of the vapour phases, and bff_1a_2 the line along which the mixed-crystal sheet of the liquid phases intersects the mixed-crystal sheet of the vapour phases.

¹⁾ By the vapour sheet of the mixed crystals we must understand here the vapour sheet coexisting with the mixed-crystal sheet.

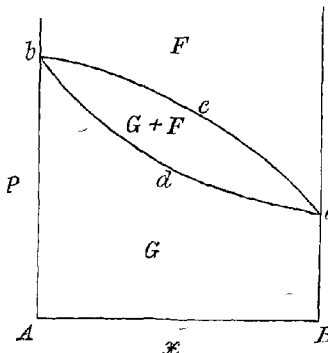


Fig. 1.

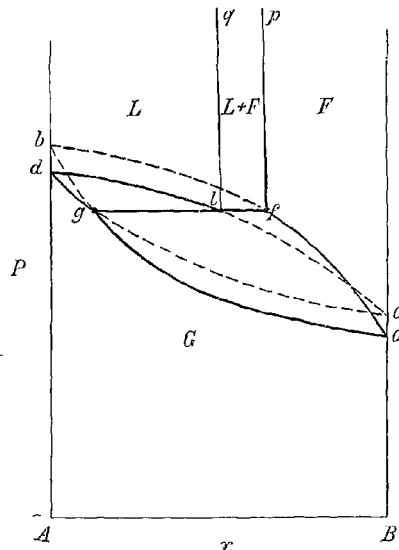


Fig 2

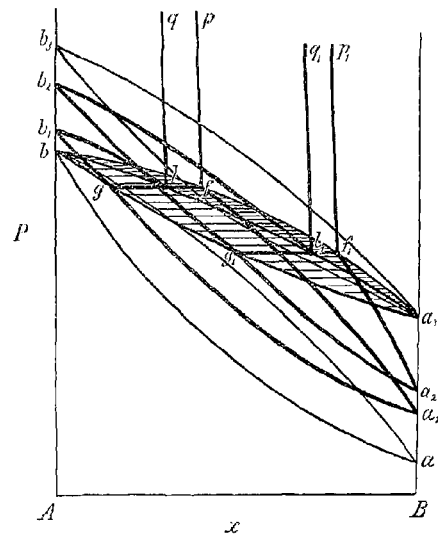


Fig 3.

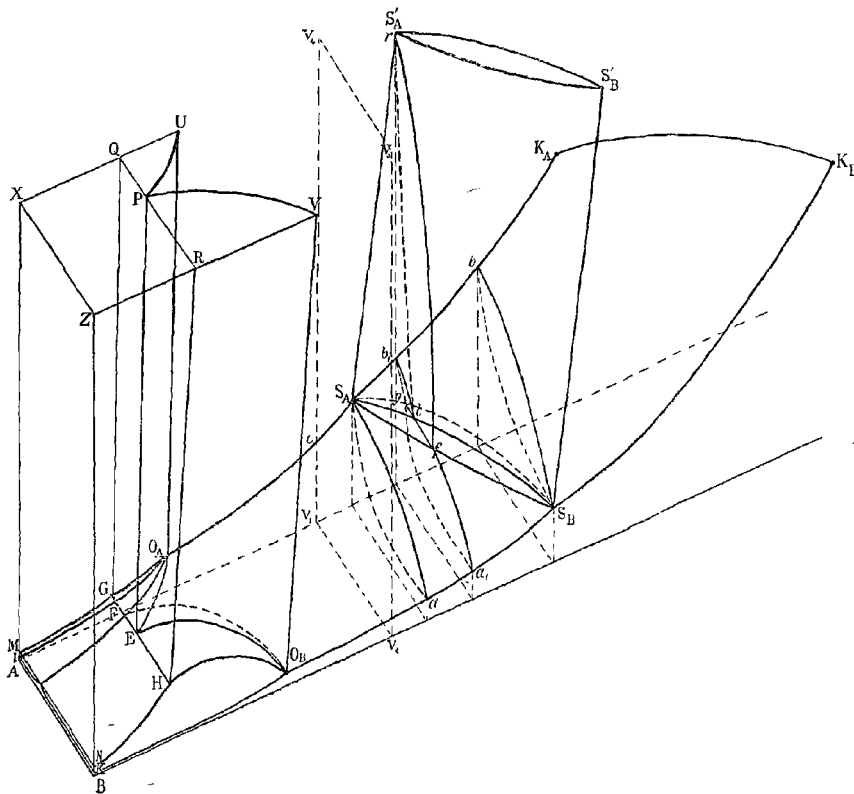


Fig 4.

All this becomes perfectly clear when we consider the spacial representation, fig. 4, to the *right* of the plane $v_1 v_2 v_3 v_4$.

S_A is the triplepoint of the component A

S_B „ „ „ „ „ „ „ B

cS_A is the vapour-pressure-line of solid A

$S_A K_A$ „ „ „ „ „ liquid A terminating in the critical point K_A .

aS_B is the vapour-pressure-line of solid B and

$S_B K_B$ „ „ „ „ „ liquid B terminating in the critical point K_B .

$S_A S'_A$ is the melting-point-line of A and $S_B S'_B$ the melting-point-line of B .

$S_A g S_B f S_A$ is the three-phase-region discussed before, and the v, x -section drawn between the triple-points S_A and S_B shows that $S_A g S'_B$ is the vapour line, $S_A l S_B$ the liquid line, and $S_A f S_B$ the mixed-crystal line.

On the two-phase-region $S_A g S_B l S_A$ lie the vapour and liquid phases which are in equilibrium with the mixed-crystals, and on the two-phase-region $S_A l S_B f S_A$ are found the liquid and the mixed-crystal phases which can coexist with the vapour.

The two-sheet surface for mixed-crystal and liquid rests on this latter two-phase-region, which surface will in general be very steep. It has been assumed in the spacial figure that as is actually the case as a rule, $\frac{dp}{dt}$ of the melting-point lines of the components is at first positive, which causes the two-sheet surface mentioned to run to higher temperatures with increasing pressure, which is here represented in an exaggerated manner.

A consequence of this situation is this that, as has been indicated in the section, at a temperature lying between the triple-point temperatures of A and B , the region for liquid and mixed crystal ceases to exist above a certain pressure, r , so that the three regions of two-phase equilibria, mixed-crystal-vapour, liquid-vapour, and mixed-crystal-liquid are limited on all sides.

It is evident that when $\frac{dp}{dt}$ is negative for both melting-point lines, point r will not lie on the melting-point line of the component A , but on that of B .

In the case that the two components pass into the fluid-crystalline state before melting, the spacial figure of such a system is represented by the whole of figure 4 for the simplest case.

The lefthand part agrees then perfectly with BAKHUIS ROOZEBOOM's spacial figure, O_A and O_B not representing the melting-points under vapour-pressure, but the transition points of the two components under vapour pressure, i. e. the points where the ordinary crystalline state passes to the fluid crystalline state under the pressure of its vapour.

If this spacial figure is cut by a plane of constant pressure, we get, at least if this pressure is chosen high enough, the simplest imaginable T - X -figure of a system of two components, each of which possesses a stable fluid-crystalline modification.

The other possible cases may be easily derived from this spacial figure.

Amsterdam June 1908.

Anorg. Chem. Laboratorium
of the University.

Physics. — "*The liquefaction of helium*". By Prof. H. KAMERLINGH ONNES. Communication N°. 108 from the Physical Laboratory at Leiden.

§ 1. *Method.* As a first step on the road towards the liquefaction of helium the theory of VAN DER WAALS indicated the determination of its isotherms, particularly for the temperatures which are to be attained by means of liquid hydrogen. From the isotherms the critical quantities may be calculated, as VAN DER WAALS did in his Dissertation among others for the permanent gases of FARADAY, which had not yet been made liquid then, either by first determining a and b , or by applying the law of the corresponding states. Led by the considerations of Comm. N°. 23 (Jan. 1896)¹⁾ and by the aid of the critical quantities the conditions for the liquefaction of the examined gas may be found by starting from another gas with the same number of atoms in the molecule, which has been made liquid in a certain apparatus. By a corresponding process in an apparatus of the same form and of corresponding dimensions the examined gas may be made liquid.

¹⁾ [Developed in view of the statical liquefaction of hydrogen and the obtaining of a permanent bath of liquid hydrogen (Comm. N°. 94 f) at which I was working then].

By [] will be designed additions made in the translation.