

Citation:

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Chemistry. — “*The metastable continuation of the mixed crystal series of pseudo-components in connection with the phenomenon allotropy*”. II. By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Sept. 26, 1914).

In the first communication on this subject ¹⁾ different possible continuations of the mixed crystal series in the metastable region have been discussed, in which chiefly the mixed crystal phases coexisting with liquid were considered.

The metastable continuation of the coexistence of two mixed crystal phases was only mentioned in a single case, where namely continuity of the mixed crystal phases in the metastable region was supposed.

It is now, however, the question what can be said of this coexistence for the case that the said continuity does *not* exist. We consider, therefore, one of the figures from 7 to 12 inclusive from the previous communication, and ask what can be predicted about the metastable continuation of the lines *p* and *m*.

On the whole a transgression of the melting temperature without melting setting in, or in other words supersolidification, is considered possible also on slow rise of temperature. The continuity discussed by VAN DER WAALS between the sublimation line *ab* and the melting

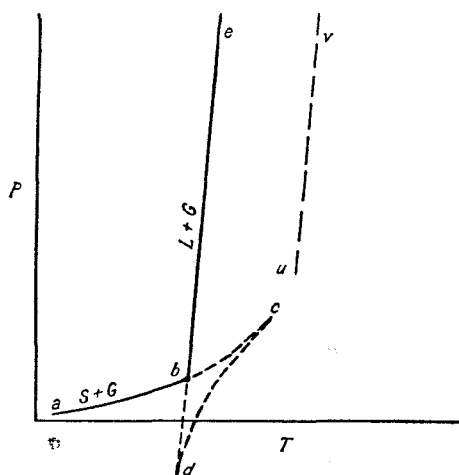


Fig. 1.

point line *bc* of a single substance, see fig. 1, starts from this supposition; we shall, therefore, also here have to take the possibility into account that the melting fails to appear at the eutectic temperature, and that the coexistence continues to exist between the two mixed crystal phases. It is, however, the question whether this possibility is limited. It follows from the continuity between the sublimation line and the melting-point line considered by VAN DER WAALS that such a limit has been assumed

for the coexistence between solid + vapour and solid + liquid.

¹⁾ These Proc. XVI p. 1167.

Above the temperature of the higher cusp e , and below the pressure of the lower cusp d , the solid substance can no longer exist by the side of the gas resp. liquid.

For our purpose the cusp c is the most important, for this point expresses that there exists a limit for the coexistence solid + gas, which implies that the orientated condition of the molecules in the solid substance coexisting with its vapour cannot exist any longer at a definite temperature, in consequence of the increasing molecular motion. If this holds for the solid substance in coexistence with vapour, there must also be a limit of existence for the solid substance *without vapour*, and as the contact with the vapour will diminish the stability of the solid state in consequence of the molecular attraction between the molecules in the solid phase and those in the gas phase, we may expect that the limit of existence of the solid substance *without vapour* will lie at a higher temperature. This temperature limit of existence will vary with the pressure, and thus we shall be able to draw a line uv in the PT -figure indicating the *limit of existence* of the solid substance.

For a binary system this holds of course, for both the components. When, therefore, we pass from the triple point of the components to the quadruple point, we get something similar. As Dr. SCHEFFER has demonstrated ¹⁾ and as is expressed in Fig. 2, the lines for $S_A + S_B + G$, $S_A + S_B + L$ merge continuously into each other

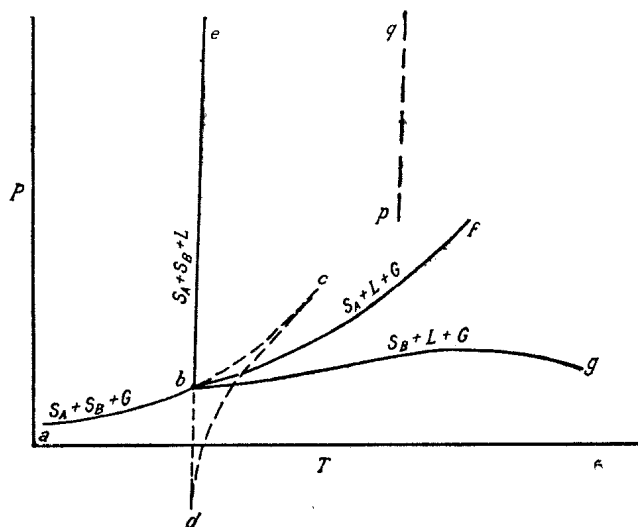


Fig. 2.

also by means of a ridge with two cusps and an unstable inter-

¹⁾ These Proc. XIII p. 158.

mediate portion, and here a line pq can be given for the *limit of coexistence* of $S_A + S_B$, because either S_A or S_B has reached its *limit of coexistence* there, which makes it impossible for the said coexistence to occur any longer.

It follows therefore from this that the lines p and m extend metastable to a definite temperature above the eutectic one.

Transition from monotropy to enantiotropy.

As is known it often happens that a substance under the vapour pressure presents the phenomenon of monotropy, whereas under higher pressure enantiotropy takes place, as has e.g. been indicated in the PT -figure 3.

The theory of allotropy again enables us to get a clear insight into the signification of this phenomenon.

Suppose the T, X -figure 4 to hold for a pressure above the triple

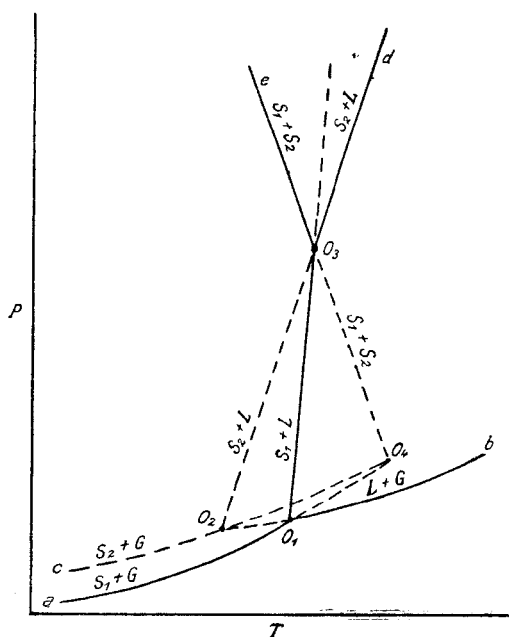


Fig. 3.

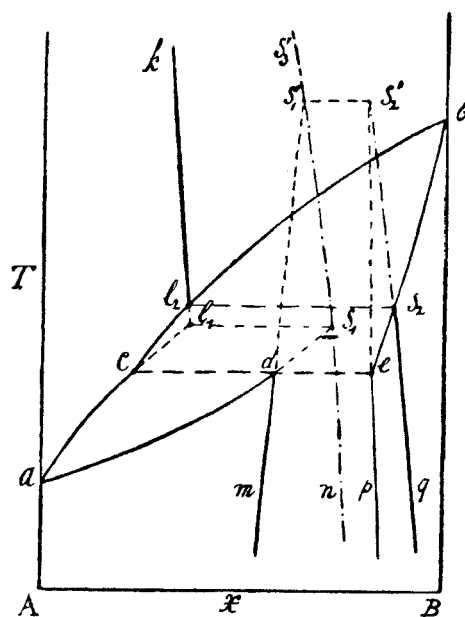


Fig. 4.

point O_1 and below the triple point O_3 , then according to the said theory the conclusion may be drawn from the fact that at higher temperature enantiotropy occurs, that the *situation of the internal equilibrium with respect to the pseudo system is dependent on the*

pressure. For only in this case e.g. the situation of the line for the internal equilibrium in the liquid with respect to the pseudo system will shift with the pressure, and if this displacement is such that the point l_2 moves downward with respect to the pseudo binary T, X -figure, l_2 will coincide with c , S_1 with d and S_2 with e at a given pressure, or in other words under this pressure two solid modifications of the unary system will be in equilibrium with each other and with their melt at a definite temperature (triple point temperature).

At this temperature the two modifications have therefore the same melting-point pressure, so that this temperature can also be called a transition temperature under the melting-point pressure.

If we raise the pressure still more, we get a T, x -figure as given in Fig. 5, from which it appears that whereas the direction of the lines for the internal equilibrium in the solid phase excluded the appearance of a stable point of transition at lower pressure, it must

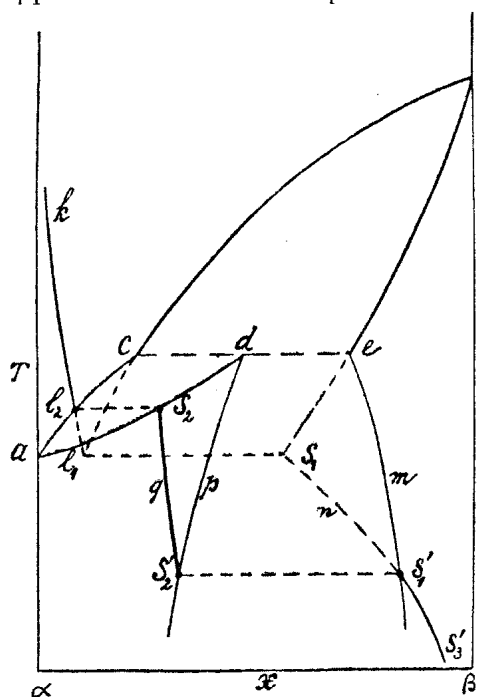


Fig. 5.

now at higher pressure necessarily lead to a transition point.

We see further that the solid phase which appears at the stable point of solidification now lies on that mixed crystal line on which the solid phase of the metastable melting equilibrium lay before, and vice versa, so that the form of crystallisation of the solid phase at the stable point of solidification will now be equal to that in which the metastable phase showed itself at a pressure below the transition pressure.

On further increase of pressure the points l_2 and s_2 move still more to the left, and the transition

equilibrium gets deeper and deeper below the equilibrium of melting. The P, T -projections of the points s_2 and l_2 , at different pressures will form the stable melting-point line, that of the point s_1 and l_1 the metastable one, whereas those of the points s'_2 , s'_1 form the transition line as indicated in fig. 3.

It therefore appears from the foregoing that the transition from

monotropy into enantiotropy can be explained in a simple way by means of the theory of allotropy.

Now the question rises where the transition line eo_2 starts from. A possibility has been given in fig. 3, from which follows that the transition line starts in a metastable point of transition under the vapour pressure O_4 . This is the view to which lead OSTWALD's¹⁾ and SCHAUM's²⁾ assumptions on the existence of a metastable point of transition *under vapour pressure*³⁾. Now it is the question whether this is the *only* possibility. It has been pointed out just now that the metastable coexistence is confined between the two mixed crystal series md and pe (see Fig. 4), and as the metastable point of transition arises by intersection of the internal equilibrium line of the solid phases with the above mentioned mixed crystal lines, it is clear that it may happen that this intersection does e.g. *not* exist under the vapour pressure.

If in such a case enantiotropy does occur at higher pressure, the transition line will proceed in a metastable way up to that pressure and that temperature at which for the first time an intersection between binary mixed crystal lines and internal equilibrium lines takes place, and there the transition line will then suddenly terminate

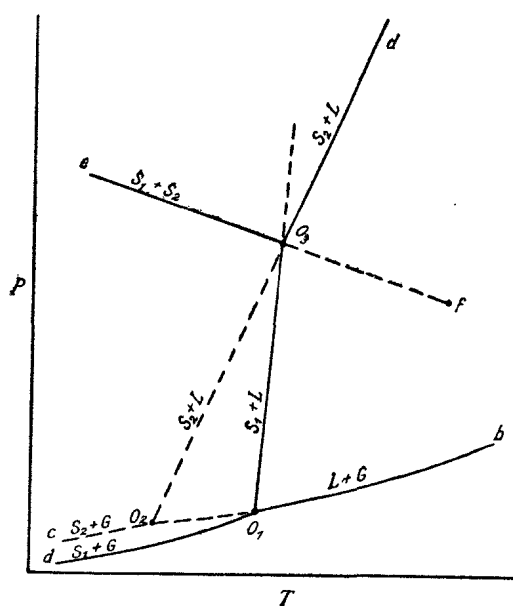


Fig. 6.

sizes, the situation of the pseudo figure will vary less with the

in a point that indicates the limit of existence of the coexistence between two solid phases which are in internal equilibrium, as fig. 6 shows.

Now it is clear that the main cause of the transition from monotropy to enantiotropy *can find* its origin exclusively in this that the situation of the pseudo figure varies more greatly with the pressure than that of the unary figure, but in by far the most cases, namely there where the pseudo components are different in molecular

¹⁾ Z. f. phys. Chem. 22, 313 (1897).

²⁾ Lieb. Ann. 300, 215.

³⁾ Cf. also BAKHUIS ROOZEBOOM, "Die Heterogenen Gleichgewichte" I, 187.

pressure than that of the internal equilibrium, and the phenomenon discussed here will have to be attributed to this superposition.

In conclusion it may be pointed out that other particularities may still present themselves, when the internal equilibrium line of the liquid phase *under the vapour pressure* lies so much on one side that there exists no metastable melting point under this pressure. If we now think that this case occurs, and that the internal equilibrium line for the liquid phase under the vapour pressure lies greatly on one side towards the right, and that this line moves towards the left on increase of pressure, we get what follows: The phenomenon of *phase allotropy*¹⁾ is wanting under the vapour pressure, monotropy *can* however, occur at higher pressure.

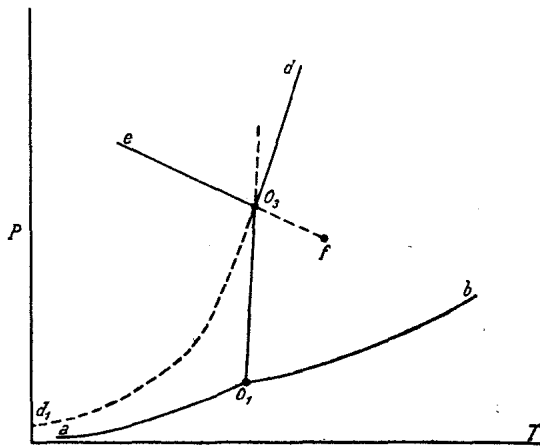


Fig. 7.

The metastable melting-point line will start at the absolute zero e.g. in the case of fig. 10 of the preceding communication²⁾, and run further as represented in fig. 7.

If on the other hand we have to do with the case of fig. 12 of

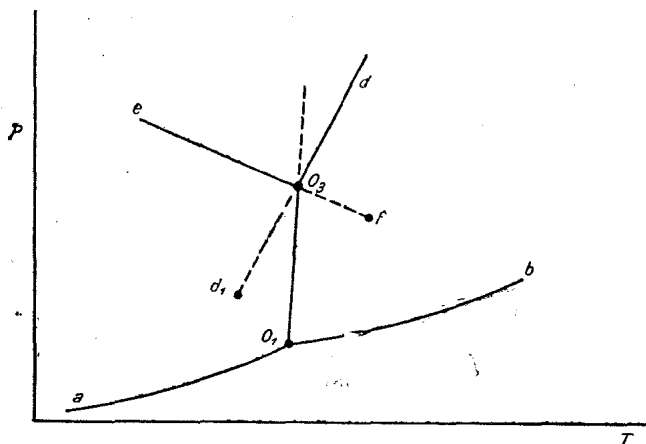


Fig. 8.

¹⁾ For the occurrence of a substance in two or more similar phases the word *phase allotropy* might be used, while the occurrence of a substance in different kinds of molecules, for which I before introduced the name *homogeneous allotropy*, might be designated by *molecular allotropy*.

²⁾ loc. cit.

the preceding communication, a *PT*-figure is possible as fig. 8 shows.

These considerations open our eyes to the possibility that enantiotropy occurs under higher pressure, notwithstanding the phenomenon of monotropy is not found *under the vapour pressure*.

Amsterdam, June 25, 1914.

Anorg. Chem. Laboratory
of the University.

Chemistry. — “*On the vapour pressure lines of the system phosphorus.*” II. By Prof. A. SMITS and S. C. BOKHORST.
(Communicated by Prof. J. D. VAN DER WAALS).

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The continued investigation of the phosphorus purposed to decide with certainty whether the red and the violet phosphorus must be regarded as two different modifications exhibiting the phenomenon of enantiotropy, as seemed to follow from JOLIBOIS’¹⁾ researches and also from our first investigations.

Confining ourselves to the communication of the result we can state with certainty that the supposed point of transition between red and violet phosphorus does not exist, and that only one solid stable modification of the phosphorus has been found, which is violet in coarser crystalline state, but red in a more finely divided state.

The vapour tensions of different phosphorus preparations approach to amounts which form one continuous vapour pressure line, when the heating is long continued.

An apparent discontinuity may arise under definite circumstances in consequence of too rapid heating. If namely, the preparation at lower temperature contains too much of the more volatile pseudo-component, too high vapour pressures are observed at these lower temperatures, in consequence of the not setting in of the internal equilibrium. In the neighbourhood of 450°, however, the setting in of the internal equilibrium becomes appreciable, and this transformation being attended with a diminution of the vapour pressure, the vapour pressure line will present a course that reminds of a discontinuity. When we worked very slowly and started from states which could only differ little from internal equilibrium states, any discontinuity had, however, disappeared.

At the same time this investigation furnished a fine confirmation

¹⁾ C. R. **149**, 287 (1909) and **151**, 382 (1910).