

Citation:

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probable that decomposition occurs at higher temperature, we must give up the study of the remaining part of the T, x -figure.

The salts which with water as second component will most likely behave as Na_2SO_4 in connection with their retrogressive melting-point line are the sulphates of *Ca, Cd, Ce, Fe, Gd, La, Mg, Mn, Nd, Ni, Pr, Sr, Th, Yb* and *Zn*, and also the salts Li_2CO_3 , Na_2SeO_4 , Na_2HPO_4 , CaCrO_4 .

It is highly probable that the same peculiar behaviour will also often be found when we choose another solvent instead of water, in which it might be possible to extend the investigation over the whole of the region of concentration for salts with low melting points on account of the absence of secondary chemical actions.

Anorg. Chem. Laboratory of the University.

Amsterdam, Sept. 1909.

Chemistry. — “*On heterogeneous equilibria of dissociating compounds*”. By Dr. F. E. C. SCHEFFER. Communicated by Prof. A. F. HOLLEMAN.

On Dec. 30th 1905 Dr. A. SMITS published a communication on intersections of the plaitpoint curve and the three-phase curve of a dissociating binary compound in these Proceedings. In this paper some of the possible cases were discussed, the phenomena described which may be expected at such an intersection, and a further systematic discussion of the remaining possibilities announced. Prof. SMITS, however, ceded the continuation to Prof. ROOZEBOOM, who proposed it to me as a subject for my dissertation; I have only been able to profit by his guidance for a short time. I gladly avail myself of this opportunity to express my thanks to Prof. SMITS for the assistance which he has given me in this investigation.

The systems, for which intersection of the plaitpoint curve and the three-phase line of a dissociating binary compound occurs, may be arranged under the six following types.

I. Both the critical end-points lie on the branch AS ; see fig. 1. This case was already discussed in the paper mentioned and illustrated by a combined PT - and xT -projection.

II. One critical end-point lies on the branch AS , the second on the branch SM , so between melting point and max. sublimation point (points p_1 and q_2 from fig. 1). From an examination of fig. 2, which represents this case schematically, it will be clear, that the

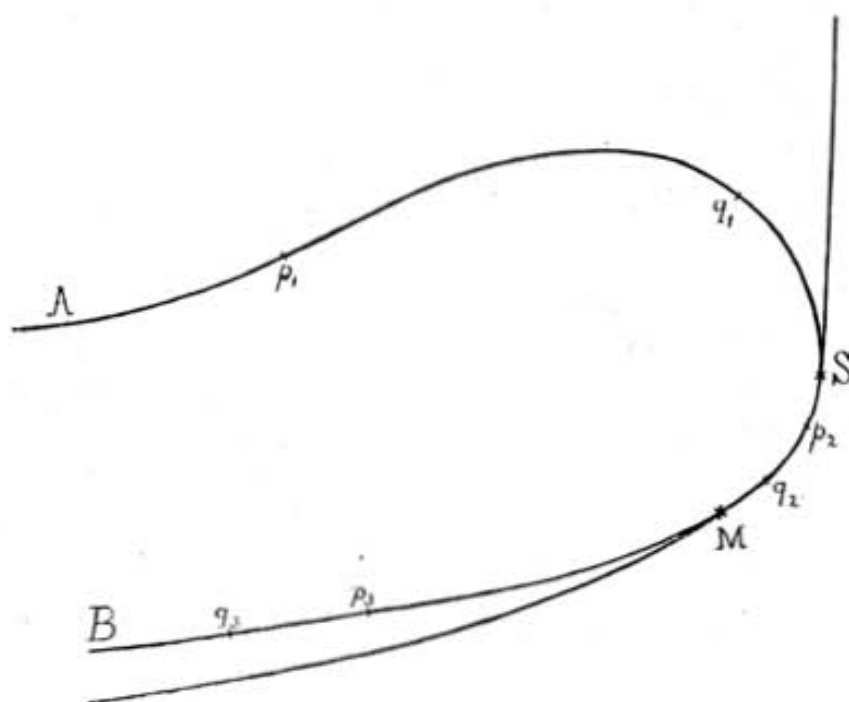


Fig. 1.

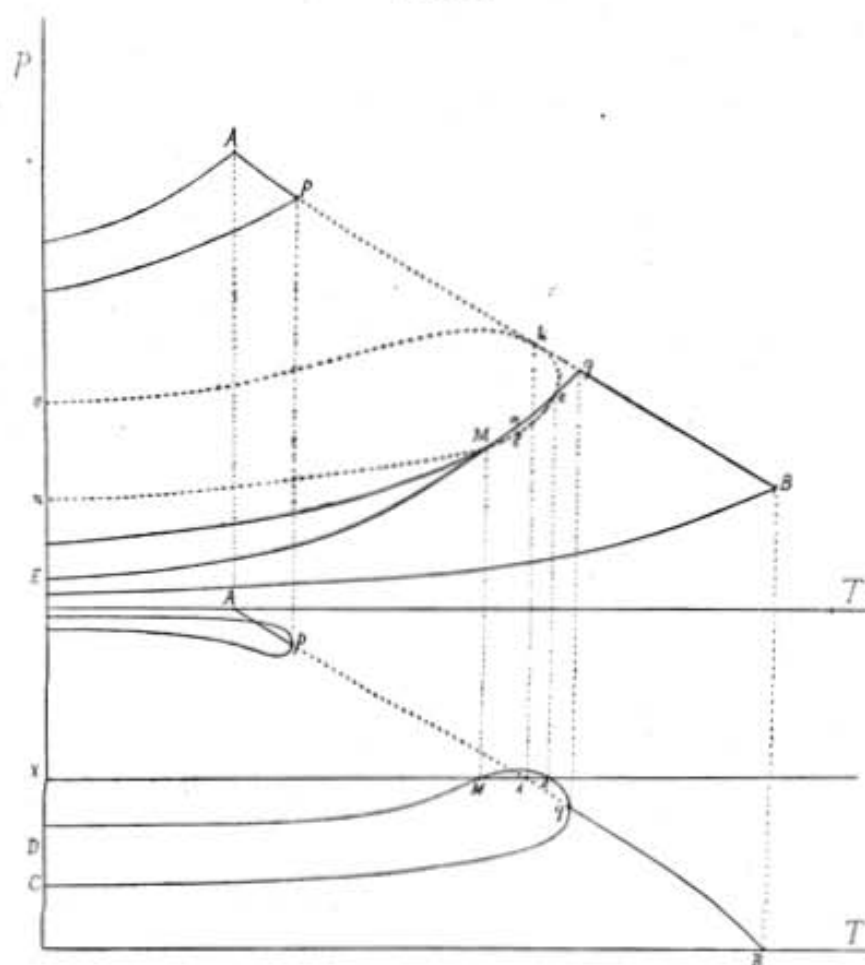


Fig. 2.

melting-point of the compound has disappeared here, that the liquid branch of the two-phase region coexisting with solid no longer cuts the line for $x = 1/2$ in the T - x -projection; the vapour branch, however, meets the latter line in two points: the maximum-sublimation point M and a point e . If in this case we examine the behaviour of the compound itself, it appears that on the line EM (P - T -projection) the solid compound exists by the side of its own vapour, that on the line Mme the three phases may occur side by side, and that the region $Mmel$ indicates the area where liquid and vapour stably coexist, while a line for solid-vapour touches the three-phase line in e , and runs towards higher temperature in the P - T -projection below eq . If the solid phase does not occur, the coexistence of L and G is moreover possible in the region $nMmeko$, to which the stable region $Mlem$ then immediately adjoins.

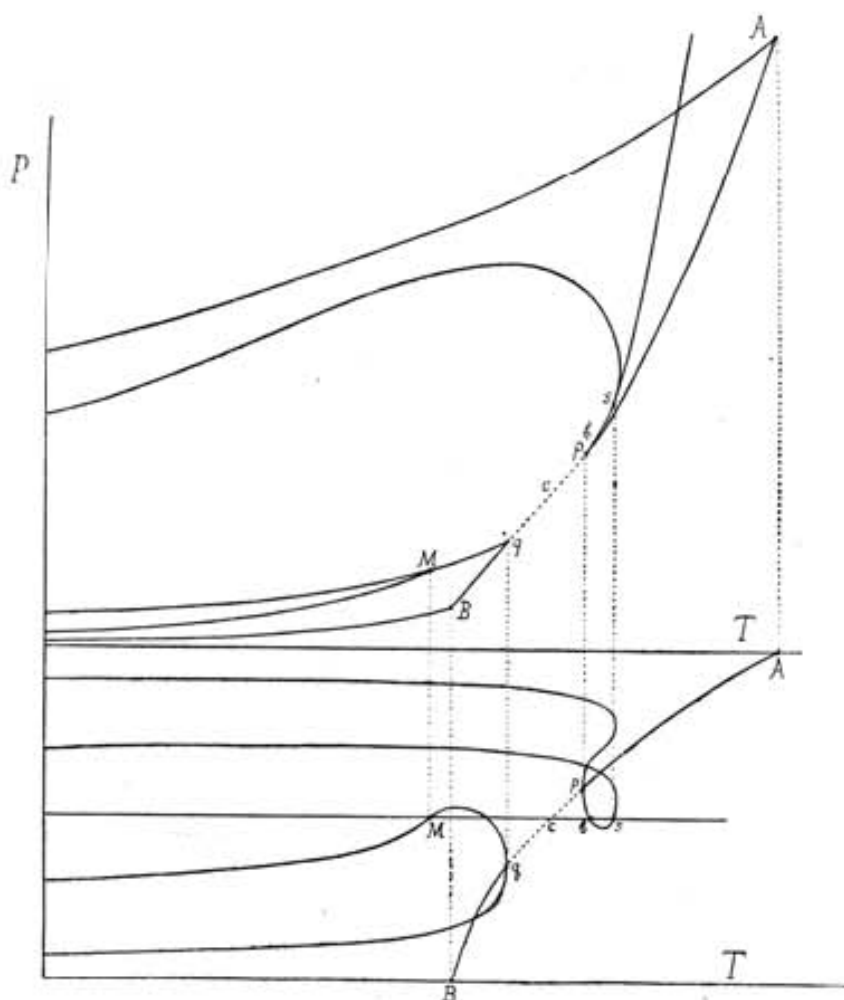


Fig. 3.

III. The two critical end-points lie on the branch SM (points p_2 and q_2 from fig. 1), so between melting point and maximum sublimation point. The liquid branch of the two-phase region of p coexisting with solid intersects the line for $x = 1/2$ twice, once in the melting-point S (Fig. 3), and the second time in a point b , which lies between S and p . In the same way the vapour branch of the region of q intersects the middle phase twice, in the maximum sublimation point M and in a point lying between M and q . In b and S the compound exists by the side of liquid of equal concentration under the three-phase pressure; in the points of intersection of the vapour branch with $x = 1/2$ by the side of vapour of equal concentration, with which then a liquid of other concentration coexists. The line which in this case indicates the equilibrium between liquid and gas for the concentration of the compound passes through S and M , but also through the two other points of intersection of liquid and vapour branch with $x = 1/2$, and through a point c of the critical line, which is, therefore metastable there.

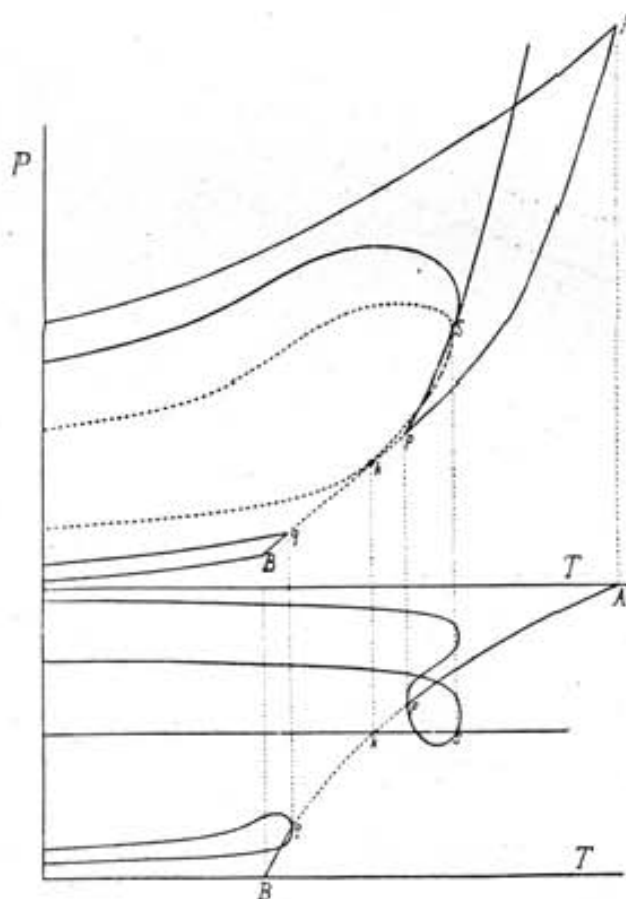


Fig. 4.

IV. One critical end-point lies on SM , the second on BM . (points p_2 and q_2 of fig. 1). In this case, which is given by fig. 4, the melting-point S still occurs on the three-phase line on the side of the first component, while the maximum sublimation point has disappeared. In connection with this is the fact that the plane of the compound is only intersected by a liquid branch; the plaitpoint k lies between p and q . In S the melting-point line touches, in the other point, where the solid compound exists by the side of liquid of equal concentration, a second line for solid-fluid, which proceeds towards lower temperature touching the three-phase line in the P - T -projection. This latter line has been omitted for the sake of clearness.

V. Both the critical end-points lie on BM (points p_2 and q_2 , fig. 1) so for concentrations which lie between those of the compound and of the second component. The equilibrium liquid-gas in the middle plane, which gave rise to a metastable critical phenomenon in the preceding case, yields here a stable critical point (fig. 5). The lines that indicate the behaviour of the mixture of the concentration of the compound, have been inserted in the figure.

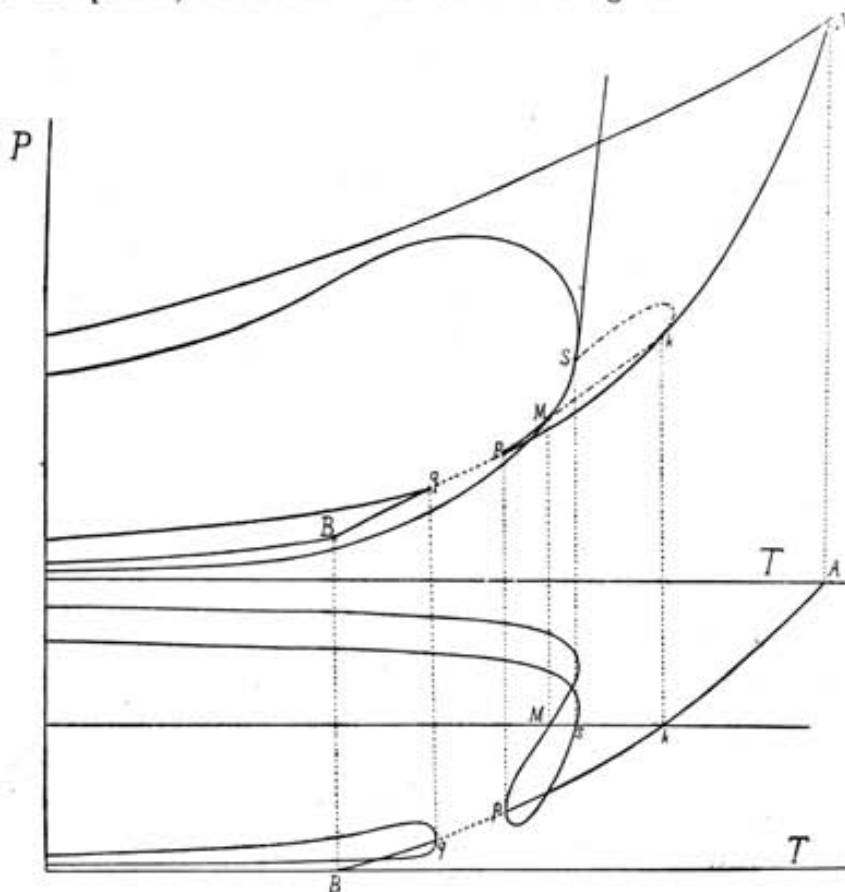


Fig. 5.

VI. One critical end-point lies on *AS*, the second on *BM* (points p_1 and q_3 of fig. 1). This case, in which both the melting-point and the maximum sublimation point have disappeared, was already discussed by Prof. SMITS in the cited paper.

The above cases, which have been derived on the assumption that the vapour pressure of the compound lies between that of the components at the same temperature, in which, therefore, the liquid-vapour surface above the melting-point gradually descends from the first to the second component, may be easily derived for systems with compounds which are less resp. more volatile than the two components, which then gives rise to the appearance of a line of minimum, resp. maximum pressure on the liquid-vapour surface. By combination of the preceding cases double intersections may occur, one of which was discussed in the cited communication.

When we consider when the cases mentioned can occur, it appears that the chance for the occurrence of case III will be the smallest, as the generally slight differences in pressure and temperature of minimum melting-point and maximum sublimation point render an intersection of three-phase line and critical line between these points improbable. So the cases II, III, and IV, where such a situation is met with, will only be rarely found, if they really occur at all; I have not succeeded in finding an instance of these cases.

The three remaining cases have this in common that they may all occur for compounds which are little soluble in one or both components. In all the systems where I have found critical end-points, this was really the case. Of the investigated systems the following belong to

Type I: Hydrochloric acid-Ammonia; Hydrogen sulphide-Ammonia;
Carbonic acid-Ammonia.

Type V: Ammonia-Sulphur dioxide.

The system hydrochloric acid-ammonia, for which it did not seem improbable that type VI would hold on account of its melting-point not being known, appeared to belong to type I, as I could ascertain that when chloride of ammonium was heated a three-phase line was found which extended from about 520°—560°.

Of these systems only that of hydrogen sulphide and ammonia is suitable for a quantitative investigation of the spacial figure, though this system, too, is open to great experimental difficulties in consequence of the action of mercury on hydrogen sulphide, which is only to be counteracted with the greatest difficulty. Yet I have succeeded

in determining one critical end-point (p); the second (q) was not to be reached on account of the pressure lying too high. Fig. 6 represents the P - T -projection of the P - T - x -figure. The three-phase line on

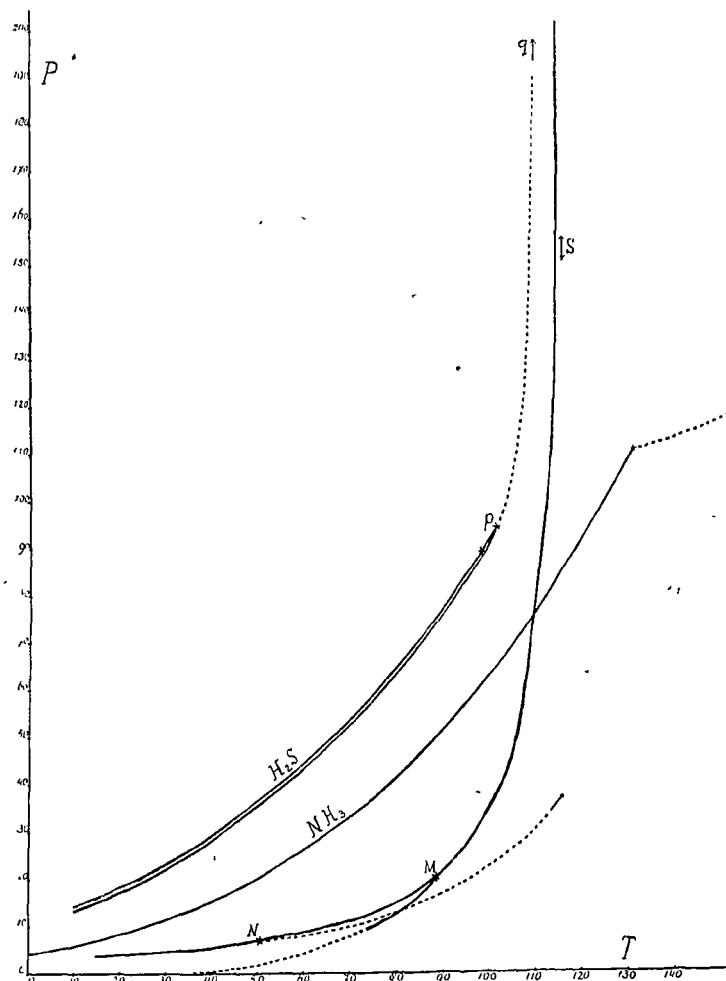


Fig. 6.

the side of the most volatile component, in our case hydrogen sulphide, practically coincides with the liquid-vapour line of the pure component; it has been drawn separate for the sake of clearness. The solubility is so slight here that the isotherm lowering of vapour-pressure (till the saturated solution under three-phase pressure is reached) is practically zero; this involves that the critical end-point p differs only little in pressure and temperature from the critical point of hydrogen sulphide ($T_{k_{H_2S}}$ 99.6°; T_{k_v} 103.0°; $p_{k_{H_2S}}$ 88.3 atm.; p_{k_p} 93.9 atm.).

The three-phase line on the ammonia side runs at low temperatures far below the liquid-vapour line of ammonia.

It ascends very rapidly in the neighbourhood of 110° , intersects the ammonia line in the P - T -projection, and runs almost vertical at 117° . I have been able to follow this line towards higher pressure to 225 atmospheres without any indication of a critical phenomenon. So the point q lies at a pressure which is higher than 225 atmospheres.

In the point N , which lies at about 50° , contact takes place of the minimum pressure line and the three-phase line. Hence the P - x -sections have a minimum pressure in the L - G -lines at temperatures above 50° . Of the sublimation line of the compound the situation in the neighbourhood of the maximum sublimation point was accurately determined; this latter point lies at 88.4° and 19.3 atmospheres; the melting-point could not be observed so accurately as a slight action of the mercury on the mixture in consequence of the generated hydrogen can give rise to a great error in the pressure; it lies at 116 à 117° , and at a pressure which is higher than 150 atmospheres.

While in the few cases in which the two points mentioned were accurately determined, the differences in pressure and temperature were slight, a difference occurs here of 28° and more than 130 atmospheres; this system is the first and only case in which such a situation was met with.

By the aid of closed tubes on one side, and Cailletet tubes on the other I have succeeded in determining the T - x -projection of the part of the critical line on the hydrogen sulphide side (fig. 7), and of the three-phase line on both sides (figs. 8 and 9).

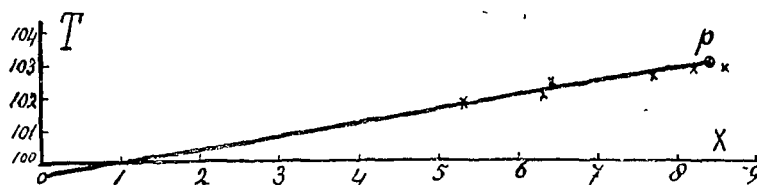


Fig. 7.

The critical line runs pretty much straight from the critical point of pure hydrogen sulphide (99.6) to the critical end-point p (103.0° , 8.4% ammonia). This line has been reproduced in fig. 8 with the liquid and vapour branch of the two-phase region coexisting with the solid compound, the former of which could be accurately determined, the latter is indicated schematically. The T - x -projection of the same region on the ammonia side (fig. 9) presents the melting-

point S (116 à 117°) at 50% of ammonia and the maximum sublimation point M (88.4°). The liquid curve was partly determined by the method of closed tubes, partly by the Cailletet method, which yielded concordant results; the dotted part, which could not be accurately observed partly on account of the mentioned disturbing reaction, partly

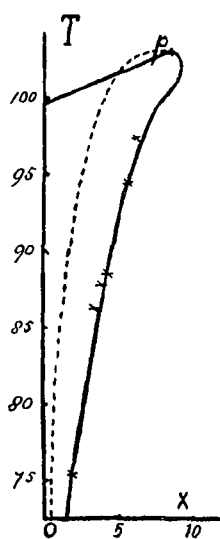


Fig. 8.

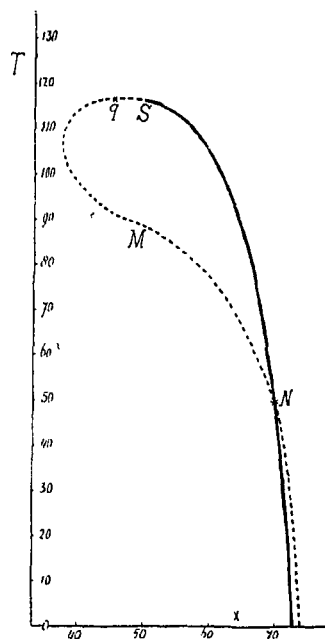


Fig. 9.

because the quantities of substance in the Cailletet tubes would have to be too small, agrees only roughly with the actual state of things with the exception of the maximum sublimation point. On the left of N the melting-point lies at higher temperature than the sublimation point, and on the other side of N the reversed situation occurs. The point N , where the two branches of the two-phase region intersect, is also to be found in the P - T -projection of fig. 6, where the minimum line of the liquid-vapour surface touches the three-phase line. With the aid of the theoretical description which Prof. SMITS gave of this case (Type I), the other lines will be clear without further explanation.