If we finally consider the relative situation of the phases on the three-phase line, it appears from what precedes that the vapour phase lies between the coexisting liquids up to the highest temperature, that the vapour branch, however, closely approaches the branch of the liquid rich in ether already before the critical end-point. It is in agreement with this that a P,x-section brought through the P,T,x-surface e.g. for the critical temperature of ether yields two curves which show decreasing values of $\dfrac{dP}{dx}$ starting from the critical pressure of ether, that the intersection with the three-phase line, however, appears just before the maximum pressure is reached, at which the concentrations of liquid and vapour would become the same.

So in the system ether-water the minimum critical temperature predicted by Prof. VAN DER WAALS lies in the immediate neighbourhood of the axis, and the remarkable point of intersection at the critical end-point.

I intend to repeat this investigation for another system hoping that I shall be able to demonstrate both peculiarities experimentally when the situation is a less one-sided one.

Anorg. Chem. Laboratory of the University.
Amsterdam, Sept. 13 1912.

Chemistry. — *"On quadruple points and the continuities of the three-phase lines."* By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

1, In a previous paper[1]) I examined the continuous connection of the three-phase lines, which occur in BAKHUIS ROOZEBOOM's spacial figure on the most simple suppositions. It then appeared that the three-phase lines $S_A + S_B + L$ and $S_A + S_B + G$ pass continuously into each other, and that in the P,T-projection this transition takes place by means of a partly metastable, partly unstable curve with two cusps, in both of which two three-phase branches touch. I have now extended this investigation to the other quadruple points which can occur in binary systems; I have, however, postponed the publication of it for a long time, because the phenomena which present themselves in the most interesting case, are much more complicated than in the above mentioned case, and a full description would require a great many intricate figures. Without treating the cases

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1) These Proc. 1910, p. 158.

fully I have, however, managed to give a survey of the phenomena which in general present themselves in quadruple points. It seems to me that the construction of the figures referring to a definite case will not present any difficulties, if this survey is consulted.

In the first place I will assume in the following considerations that continuity only takes place between liquid and gas phases. So I preclude an eventually present continuity between solid and fluid. If it should appear that VAN LAAR's theory, which leads to this continuity, is valid, this transition will also have to be reckoned with for a complete treatment. On the appearance of a quadruple point $S_1 + S_2 + S_3 + S_4$ the four solid phases could then pass continuously into each other. Until, however, the existence of the continuity in question shall have been experimentally realized, it seems better to me not to take it into account to prevent our entering into an elaborate consideration of a great many cases which may appear later on to be physically impossible.

In the second place I exclude a continuity between solid phases. Their occurrence has indeed been ascertained, but until certainty has been obtained as to how the crystallographic orientation in the equation of state of the solid substance is to be taken into account, it seems impossible to me to obtain certainty about the connection of the three-phase lines in consequence of this continuity.

If we now consider that in a binary system unmixing in the gaseous state has never been found as yet, and never more than two simultaneous liquid layers, it appears that in all six different quadruple points can occur:

1. $S_1 + S_2 + S_3 + S_4$ 3. $S_1 + S_2 + L_1 + L_2$ 5. $S_1 + S_2 + L + G$

2. $S_1 + S_2 + S_3 + L$ 4. $S_1 + S_2 + S_3 + G$ 6. $S + L_1 + L_2 + G$

In the quadruple points 1, 2, and 4 no continuities can appear between the three-phase lines, in which liquid and gas phases participate. Of the three cases 3, 5, and 6, which accordingly remain for our consideration, the case 5 has already been fully examined in the cited paper.

Case 3 only differs slightly from 5. In the quadruple point 3 the the three-phase lines $S_1 + S_2 + L_1$, $S_1 + S_2 + L_2$, $S_1 + L_1 + L_2$ and $S_2 + L_1 + L_2$ occur, of which only the two first are in continuous connection with each other. It is easy to see by the aid of the V,x-projection, that this connection again takes place by means of an unstable branch with two cusps in the P,T-projection, just as this

was shown before for the case **5** with regard to the three-phase lines $S_1 + S_2 + L$ and $S_1 + S_2 + G$ [)].

If, however, we compare the three-phase lines $S_1 + L_1 + L_2$ and $S_2 + L_1 + L_2$ of case **3** with the corresponding lines S_1+L+G and $S_2 + L + G$ of case **5**, it is clear that in the latter case the two lines terminate in the melting-points of the two components, at least if we have a case of the ordinary spacial figure. In case **3** on the other hand, the binodal line of the two liquids can be an entirely closed curve with two plaitpoints. Each of the three-phase lines $S_1 + L_1 + L_2$ and $S_2 + L_1 + L_2$ will then possess two critical end-points in the P,T-projection. Yet this difference between the cases **3** and **5** is not so great as one would be led to expect at first sight. The occurrence of critical end-points is not confined to the case **3**; also in case **5** it is possible that the three-phase lines $S_1 + L + G$ and $S_2 + L + G$ do not reach the melting-point, but come into contact with a critical line. This case, which is pretty well the prevailing one in case **3**, has been shown by SMITS for case **5** in the system ether-anthraquinone.

2. *The quadruple point* $S + L_1 + L_2 + G$.

So we have seen that the quadruple points **3** and **5** give rise to analogous phenomena; the only remaining case **6**, however, deviates from what we discussed in many respects. Where in the quadruple points **3** and **5** continuity is always only possible between two phases we have three phases L_1, L_2 and G, in the quadruple point **6**, which all three may pass continuously into each other. So the phenomena become more complicated here, and it is already a priori clear that the connection between the three-phase lines may take place in different ways. What cases we have to distinguish for this quadruple point can be easily derived from Prof. VAN DER WAALS' investigations on unmixing. It is known that the critical line can present very different shapes when a longitudinal plait exists on the ψ-surface.

In the first place we may imagine that at low temperature solely a transverse plait occurs on the ψ-surface, that on rise of temperature a longitudinal plait is formed (inside the transverse plait), that on further rise of temperature it makes its way outside the transverse plait, and that it afterwards again retreats inside the plait, and disappears at a temperature which lies lower than the lowest critical temperature of the transverse plait. This case, to which we shall

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[)] Cf. also § 3.

refer as the first in our further considerations, yields a critical line, which consists of two entirely detached portions, one of which, lying at high temperature, presents the normal shape, and the other is in the P,T-projection a closed figure with two heterogeneous double plait-points, which represents the locus of the critical points of the longitudinal plait.

In the second place it is possible that the longitudinal plait, which has got outside the transverse plait in the same way as above, continues to exist far above the temperature at which the transverse plait gets detached on one of the two sides. Then a transition takes place at a certain temperature in the connection of the plaits; the longitudinal plait, which was entirely closed at low temperature, then merges into a part of the transverse plait, while simultaneously the portion of the transverse plait on the side of the component with the lower critical temperature gets isolated, and retreats inside the former at rise of temperature, and disappears. This case is referred to as the second in what follows.

I have now examined the question what phenomena may appear, when a tangent plane for solid-fluid is rolled over the ψ-surfaces in question, and it has appeared to me that the behaviour in both cases can be ascertained by a comparatively simple train of reasoning. In these considerations I have confined myself to those cases, for which only the components occur as solid substances.

3. *The first case.*

When we consider the case that was called the first in the preceding paragraph, we can get a survey of the phenomena by means of figure 1. In this figure it has been assumed that $(dp/dx)_v$ is always positive, in other words that we are in the lefthand part of the isobaric figure. The longitudinal plait here possesses two critical points P_1 and P_2 where contact takes place with the spinodal line. Further only the liquid binodal line has been drawn of the transverse plait; the vapour branch, which lies at large volumes has been omitted in the diagram; it possesses a ridge, the two end-points of which indicate the phases coexisting with A and B. About the relative situation of longitudinal and transverse plait we know that at low temperature the longitudinal plait lies entirely inside the transverse plait, at higher temperature the former passes the border of the transverse plait, and at still higher temperature it retreats again inside the latter. In this temperature range the transverse plait covers the whole width of the figure, as we remain all the time below the critical temperature of the components.

We shall now imagine that a tangent plane for solid-fluid rolls over the ψ-surface, and we choose as solid substance the first com-
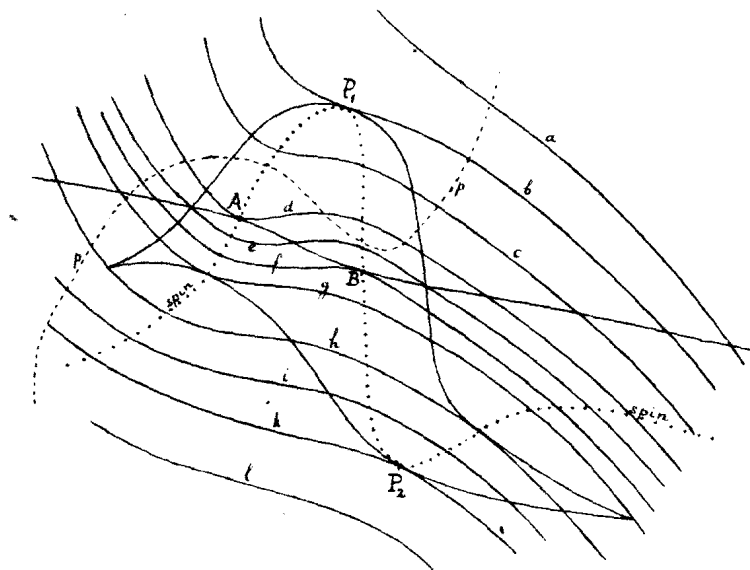

Fig. 1.

ponent. At very low temperature the curve which is described by the tangent plane on the ψ-surface, will lie entirely on the right-hand side of the figure. So it will not come in contact with the longitudinal plait, if it should be present already. This condition has been represented by the curve a in figure 1 ; it intersects the binodal of the transverse plait, and this point of intersection indicates the liquid of the three-phase equilibrium $S + L_2 + G$ (we denote by L_2 the liquids lying on the righthand of the longitudinal plait). Now on rise of temperature the possibility presents itself that the binodal solid-fluid comes in contact with the longitudinal plait. If this is the case contact will take place, and this can happen no-where else than in the plaitpoint. This is easy to see, as in case of contact in another point of the longitudinal plait a second liquid would have to coexist with the solid substance, and so no contact, but intersection would have to take place. This condition of contact has been represented by curve b. So the fluid phases coexisting with solid yield a line b, which passes through the stable plaitpoint of the longitudinal plait, and intersects the transverse plait in two points, of which again only the liquid point has been indicated in fig. 1.

Then at higher temperature an intersection follows in four points. Two points of intersection with the longitudinal and two with the transverse plait then lie on the line solid-fluid; so at this tempera-ture there are two stable three-phase equilibria $S + L_1 + L_2$ and

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S + L$_2$ + G (line c); the equilibrium L$_1$ + L$_2$ + G is still metastable. This condition continues to exist till the line for the fluid phases coexisting with solid gets into contact with the liquid branch of the transverse plait in A, and then also passes through the righthand cusp in the vapour branch of the transverse plait (line d). This is followed by a range of temperature, in which six points of intersection with the transverse plait, and still two with the longitudinal one occur. At these temperatures five three-phase equilibria then appear in all. This range terminates at the temperature of the curve f, where again contact with the liquid branch of the transverse plait is found (in B), and the line for fluid by the side of solid passes through the lefthand cusp of the vapour binodal curve. In this temperature range we find the quadruple point, the behaviour of which is given by the curve e. Above this range of temperature four points of intersection again occur, till the temperature is raised to that of g, where contact with the longitudinal plait takes place. Then eight points of intersection again follow, six of which, however, now lie on the longitudinal plait. This continues to be so till the condition h is reached, above which again two intersections with the longitudinal, and again two with the transverse plait take place (curve i). At last in k the temperature is reached at which contact in the hidden plaitpoint P_2 takes place. At still higher temperature
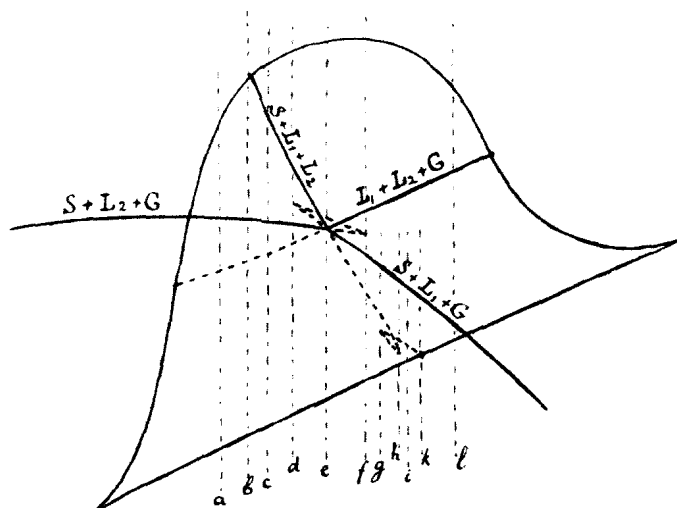

Fig. 2.

there is no longer contact of the fluid line with the longitudinal plait, and the latter will recede within the transverse plait.

After this discussion it will be easy to construct the P,T-projection of the three-phase lines, which has been given in fig. 2. The tem-

peratures for which the intersections in fig. 1 were studied, have
been indicated in fig. 2 by the same letters. The three-phase line
$L_1 + L_2 + G$ retairs therefore the shape which it has when no
solid substance occurs; one part has, however, become metastable
here. Just as the line $L_1 + L_2 + G$ the three-phase line $S + L_1 + L_2$
possesses two plaitpoints, one of which is stable, and the other
metastable or unstable. Besides the former possesses a ridge, which
lies entirely in the non-stable region, the ends of which correspond
with the points where the lines g and h of fig. 1 cut the spinodal
curve. The two other three-phase lines $S + L_1 + G$ and $S + L_2 + G$
are continuously connected by means of such a ridge, the end-points
of which correspond with the points A and B of fig. 1. That really
ridgelike figures occur here, with contact of every time two branches
in the end-points is easy to see; this will always be the case when
two binodal lines touch in a point of the spinodal line (plaitpoints
excepted). If we choose the temperature very little different from that at
which contact takes place, then if the direction of the change of tempe-
rature has been correctly chosen, an intersection will appear of the bino-
dals; then in the Γ, x-figure there are two three-phase-triangles present,
the angular points of which draw near to each other on approach of the
temperature of contact, and coincide when this temperature is reached.
If e. g. we have the intersection of a line between d and e with the
transverse plait in fig. 1, then the two phases L_1, the two phases
G, and the two solid phases will coincide at a lower temperature.
Now the value for $\dfrac{dp}{dT}$ for both the two three-phase equilibria is
given by the equation :

$$\frac{dp}{dT} = \frac{\eta_{GL_1} - \dfrac{x_G - x_{L_1}}{x_S - x_{L_1}} \eta_{SL_1}}{v_{GL_1} - \dfrac{x_G - x_{L_1}}{x_S - x_{L_1}} v_{SL_1}},$$

in which all the quantities of the second member refer to the three
coexisting phases. It is now clear that on approach of the tempe-
rature of contact the two phases L_1, the two phases G, and the
two solid substances differ less and less in properties, and that at
the temperature at which contact takes place, the quantities of the
second member refer to identical phases. For the two three-phase
branches the value of $\dfrac{dp}{dT}$ becomes exactly the same at the tempe-
rature of contact, and so contact occurs.

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It may be further pointed out that the value of $\dfrac{dp}{dT}$ at this contact does not in general become infinitely great. This would be the case, if in the point of contact also the condition:

$$\frac{v_G - v_{L_1}}{x_G - x_{L_1}} - \frac{v_S - v_{L_1}}{v_S - v_{L_1}} = 0 \;{}^{.)}$$

was satisfied.

It is easy to see from fig. 1 that this will not be the case in the point A.

4. In § 3 we assumed a very decided relative displacement of the fluid line with respect to the longitudinal plait for the derivation of fig. 2. It will be clear that the relative displacement of the said binodal curves can also take place in another way than that described above. If we want to ascertain how great the number of possibilities is that may occur, we should first of all bear in mind that our first assumption was, that $\left(\dfrac{dp}{dx}\right)_v$ was positive on the ψ-surface. Further we took the first component as solid substance. If we now exclude the appearance of a line $\left(\dfrac{dp}{dx}\right)_v = 0$, it will be clear that we can survey all the cases if we take $\left(\dfrac{dp}{dx}\right)_v$ always positive, and choose the two components as solid substances. For if $\left(\dfrac{dp}{dx}\right)_v$ is negative, and the solid substance is the second component, we get the same phenomena as in the case where $\left(\dfrac{dp}{dx}\right)_v$ is positive, and the first component appears as solid phase.

So if we keep $\left(\dfrac{dp}{dx}\right)_v$ always positive, the situation of the longitudinal plait is always as indicated in figure 1. The differences between the cases which may occur, are accordingly caused by the fact that both components can occur as solid phase, and by the relative displacement of the solid-fluid line with respect to the longitudinal plait.

If we confine ourselves to the case that the first component is the solid phase, we see a second possibility in figure 1, if we suppose

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[1]) The transformed denominator of the above expression for $\dfrac{dp}{dT}$.

that the line for solid-fluid retains its shape a to higher temperatures, and that then on rise of temperature a longitudinal plait arises on the righthand of a, which plait extends and overtakes the line for solid-fluid. It is clear that then contact takes place in the unstable plaitpoint P_2 at low temperature, and that with rising temperature the intersections with the longitudinal plait may take place in reversed order as has been described above. In this case in opposition to fig. 2 the three-phase line $L_1 + L_2 + G$ is stable at temperatures below the quadruple point, and at temperatures above it metastable, and the stable part of $S + L_1 + L_2$ possesses a positive value for $\frac{dp}{dT}$. This, however, does not affect the connection between the three-phase lines $S + L_1 + G$ and $S + L_2 + G$, and the two other three-phase lines retain their critical points just as in fig. 2.

Finally we may assume that the line for solid-fluid forces its way inside the longitudinal plait in the way represented in fig. 1 by the line p, and this line can again be displaced in two directions with respect to the longitudinal plait, so that either the stable or the metastable plaitpoint is situated at the lower temperature.

So we get in all four different quadruple points, when the solid substance is the first component, and as many when the second component appears as solid substance, so that we have to conclude to eight different types of quadruple points, at least if we disregard the appearance of ordinary pressure and temperature maxima, which occur, if the situation of the three-phase points satisfies the conditions:

$$\frac{\eta_2 - \eta_1}{x_2 - x_1} - \frac{\eta_3 - \eta_1}{x_3 - x_1} = 0 \text{ resp. } \frac{v_2 - v_1}{x_2 - x_1} - \frac{v_3 - v_1}{x_3 - x_1} = 0.$$

I will not enter into the further treatment of these cases, because for all these possibilities the result already obtained in § 3 always remains intact that the two three-phase lines $S + L_1 + G$ and $S + L_2 + G$ are in continuous connection, and that on the two other three-phase lines two critical points occur. Nevertheless it seemed desirable to me to give a survey of these possible cases, because the appearance of these quadruple points will not be rare; they will occur in almost any system where unmixing continues to exist below the melting-points of the components.

5. *The second case.*

In the second case we have supposed that the longitudinal plait continues to exist to above the lower critical temperature of the transverse plait. So one of the components has then become critical,

and at these temperatures only the appearance of the other component as solid phase is possible. So again supposing $\left(\dfrac{dp}{dx}\right)_v$ to be positive, only the first component can appear as solid substance because then the second component will generally possess the lower critical temperature. We know that in this case a transformation in the connection of the plaits takes place, as is indicated in fig. 3. We must now suppose that at low temperatures the behaviour does not
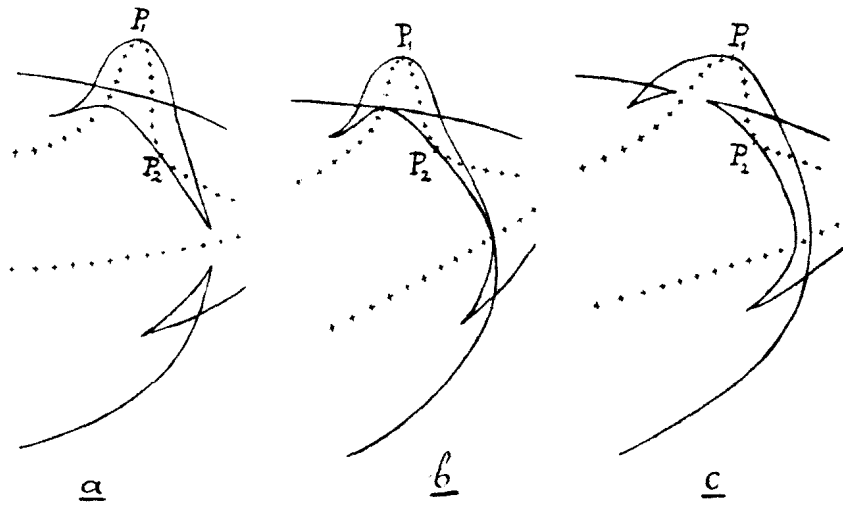

Fig. 3.

differ from what was discussed in § 3 (lines a, b, and c of fig. 1), that then, however, the transformation of fig. 3 makes its appearance. If this takes place before the condition g of figure 1 has been reached, it is clear that the liquid points of the three-phase line $S + L_1 + L_2$ lie on the longitudinal plait at low temperature, but that when the transformation takes place the branch on which L_1 and L_2 lie gets into connection with the vapour branch. Hence on rise of temperature the three-phase line $S + L_1 + L_2$ merges continuously into $S + L_1 + G$. Then the points L_2 and G of the three-phase line $S + L_2 + G$ which lie on the transverse plait at low temperature, are both found on the closed portion in the transformation; hence the three-phase line $S + L_2 + G$ terminates in the hidden plaitpoint P_2, where the line for fluid by the side of solid touches the closed portion. Without our entering into any further particularities, it will be clear in my opinion, that fig. 4 indicates the P,T-projection holding for this case. That again a transition takes place by means of an unstable ridge, can be shown in perfectly analogous way as in the transition described in § 3.
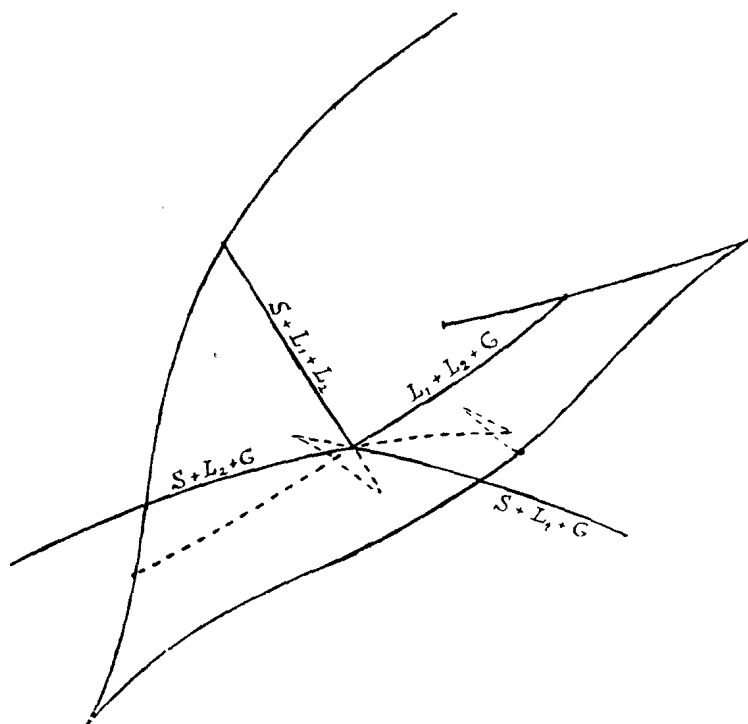
Fig. 4.

6. It will be clear that the number of cases possible compared with those of the first case of § 3 and § 4 will be smaller here, as only one of the components can appear as solid substance, but that on the other hand the transformation of the plaits gives rise to a complication.

If we again take the case of § 5, the transformation can take place before the state g has been reached, as described above. If, however, the temperature of g is lower than that of the transformation, then just as before, the three-phase line $S + L_1 + L_2$ continues to terminate in the hidden plaitpoint P_2, and so, though the shape of the critical line is entirely different from that in § 3, we have the same connection of the three-phase lines $S + L_1 + G$ and $S + L_2 + G$, and two critical points on $S + L_1 + L_2$ and $L_1 + L_2 + G$.

In analogy with § 4 we can also imagine that the longitudinal plait makes its appearance and is transformed after the solid-fluid line in the figure has been shifted some distance to the left, and then overtakes the solid-fluid line. In this case we shall again have to distinguish two cases, viz. that the transformation appears before or after the state g.

In the first case the three-phase line, which begins in the unstable

plaitpoint, will terminate in the critical point P_2 of the transverse plait, which has detached itself from the side, and a stable critical end-point occurs with the properties described by SMITS in the system ether-anthraquinone. The three-phase line $S + L_1 + G$ then merges continuously into the three-phase line $S + L_1 + L_2$. If, however, the transformation takes places after the state g, the three-phase line that has started from P_2 will pass into $S + L_1 + L_2$, and terminate in the stable plaitpoint P_1. Then the three-phase lines $S + L_1 + G$ and $S + L_2 + G$ are continuously connected, and the latter ends again in a critical end-point on the closed transverse plait, which has detached itself.

Finally we should still take into account the possibility that the line for fluid can possess the shape of line p in fig. 1, and also for this case we get four types of quadruple points, which, however, differ only slightly from the preceding types.

All the possibilities, however, agree in this that either two critical points occur on the three-phase lines $S + L_1 + L_2$ and $L_1 + L_2 + G$, and the continuous connection takes place between $S + L_1 + G$ and $S + L_2 + G$, or one of the three-phase lines $S + L + G$ is in connection with $S + L_1 + L_2$, and the other three-phase line $S + L + G$ possesses one or two critical points.

7. In the preceding paragraphs we have pretty completely discussed the types which can possess quadruple points, in which the components occur as solid phases. The occurrence of mixed crystals and compounds does not give rise to essential modifications. All the same different types should be distinguished for these cases; this follows, namely, already from the fact that with the discussed quadruple points the solid substances always possess either the greatest or the smallest concentration, and so the possibility was excluded that the concentration of the solid substance lies between that of the coexisting liquid and vapour phases. To form an opinion of these cases the most rational way would be to have recourse to the ψ-surface; this alone can give a complete insight into the peculiarities that occur for a definite case. Generally, however, we can avoid this course; but then the danger is great to assume possibilities, which would appear to be physically impossible if the ψ-surface was consulted. To escape this danger, and to avoid on the other hand the more laborious way via the ψ-surface, I will here draw attention to a rule which gives a relation between the relative situation of the three-phase lines and the concentrations of the coexisting phases.

The simplest way to state this rule is in my opinion as follows.

The region that does not possess metastable prolongations of three-phase lines in the P,T-projection is that of coexistences of phases of consecutive concentration.

Perhaps the clearest way to set forth the meaning will be by means of fig. 2.

If we produce the four stable three-phase lines through the quadruple point, as has been done in fig. 2, it appears that no metastable prolongations occur in the region between $S + L_1 + L_2$ and $L_1 + L_2 + G$. The region in question indicates the coexistence of $S + L_1$, $L_1 + L_2$ and $L_2 + G$. These coexistences refer every time to two phases consecutive in concentration, i. e. if the four phases are arranged according to their x-values, the succession is $S L_1 L_2 G$. That this is really the case in fig. 2, is clear since it has been assumed there that $\left(\dfrac{dp}{dx}\right)_c$ is positive, that by L_1 the liquids were denoted which lie on the lefthand of the longitudinal plait, and that the first component appears as solid substance.

8. To prove the rule in question we will indicate the phases arranged according to their x-values in the quadruple point, by 1, 2, 3, and 4, so disregarding altogether what state of agregation the phases possess. The four three-phase lines $1 + 2 + 3$, $1 + 2 + 4$, $1 + 3 + 4$ and $2 + 3 + 4$ divide the space round the quadruple point in the P,T-projection into four parts, which every time indicate pressures and temperatures of two-phase regions. We know besides that every three-phase line forms the boundary of three two-phase regions, and so that on one side of the three-phase line one, on the other side two regions occur, where every time a combination of two of the three phases are in equilibrium. In the first place it is now clear that none of the two-phase regions can have an angle at the quadruple point which is greater than 180°. If this were so we should be able to produce one of the bounding three-phase lines through the quadruple point. This metastable prolongation would then lie in the region where two of the three phases could coexist in a stable way; then, by the side of these two the third could also occur stable on the three-phase line, which is evidently impossible, because the prolongation represents metastable states.

Every quadruple point which contains a two-phase region with an angle that is larger than 180° is therefore impossible. If we take this into account, the thesis in question can be simply derived. For this purpose we first take the coexistence of the phases with the

extreme x-values, so 1 and 4, then the two-phase region $1 + 4$ will occupy all the available width in the spacial figure; this region forms a space which has the full width of the four-phase line as boundary. So with the same pressure and temperature no other stable two-phase equilibrium is possible there. The two other two-phase equilibria $1 + 2$ and $2 + 4$, which lie by the side of the three-phase line $1 + 2 + 4$, and the equilibria $1 + 3$ and $3 + 4$, which lie by the side of the line $1 + 3 + 4$, lie therefore always on the other side of the lines in question in the $P,-T$ projection.
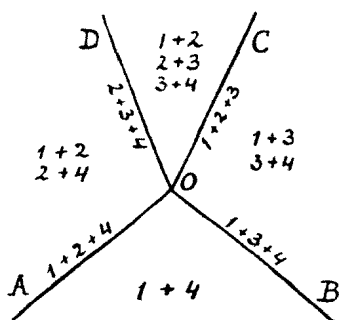

Fig. 5.

So in fig. 5 the situation of the region $1 + 4$ determines that of the two three-phase lines AO and BO, and at the same time that of the regions $1 + 2$, $2 + 4$, $1 + 3$, and $3 + 4$. So it now remains to decide what the situation is of the two remaining three-phase lines. It is now easy to see that the line OC lying on the right must represent the coexistence of $1 + 2 + 3$ and the line OD that of $2 + 3 + 4$. The line OC, namely, must bound on one side either the region $1 + 3$ or the region $3 + 4$. This can only take place by the three-phase line $1 + 2 + 3$, because in the other case besides $3 + 4$, also the region $2 + 3$ would have to lie on the same side of the three-phase line, which can evidently not be the case. So now, the situation of the phases is quite determined. So it appears that one two-phase equilibrium occurs in the region AOB, two in the regions BOC and DOA, and three in COD.

Now the angle AOB must contain the metastable prolongations of the two three-phase lines CO and DO. Suppose namely, that the prolongation of CO should fall in DOA, then the region $1 + 2$ should present an angle which is greater dan $180°$; if the prolongation of DO lay in COB, then the region $3 + 4$ would possess an angle greater than $180°$. So it has been proved that only such a situation is possible that no prolongation falls in the angle COD. And this proves the stated rule.

It will, moreover, be clear from the above proof, that the thesis might also be stated as follows :

If the phases, arranged according to their x-values, are expressed by 1, 2, 3, and 4, the angle without metastable prolongations lies between the three-phase lines $1 + 2 + 3$ and $2 + 3 + 4$.

9. The application of this rule can naturally be twofold. At

certain values of the concentration it is easy to distinguish, what quadruple points can occur and what cannot. And in the second place it furnishes a simple means to read directly the consecutive order of the concentrations from the observations of the three-phase lines.

The former kind of applications is of course far more numerous than the second. There are, namely, only few cases as yet, in which the situations of all four three-phase lines at the quadruple point are determined.

To elucidate the former kind of applications, I will briefly examine what the rule requires for some known quadruple points. The quadruple point of the ordinary spacial figure, in which the succession of the phases is $S_1 G L S_2$, has to fulfil the demand that the region between $S_1 + G + L$ and $G + L + S_2$ does not contain metastable prolongations.

If we consider the quadruple point of two salt-hydrates by the side of liquid and vapour, in which the order of the concentrations is $G L H_1 H_2$, the rule in question demands that no metastable prolongations occur between the three-phase lines $G + L + H_1$ and $L + H_1 + H_2$. This rule both holds for the ordinary case that the hydrate H_1 rich in water is transformed into that which is poor in water on rise of temperature and for the "inverse melting-points", where the reverse takes place. For the former case the rule requires among others that the prolongation of $H_1 L G$ lies at lower pressure than the stable part of $H_2 L G$, and reversely, which must really be the case, as is known.

What type of quadruple points must be expected in the case of an "inverse melting-point", will be discussed a little more fully here.

If we think the transformation of the two salt-hydrates to take place in such a way that the one rich in water exists at higher temperature than that poor in water, then the quadruple point will have to satisfy besides the above-mentioned demand, also the condition, that at temperatures below the quadruple point the three-phase line $G + L + H_2$, above it the line $G + L + H_1$ is stable. If we further consider that on the three-phase line $L + H_1 + H_2$ the transformation $H_2 + L \rightarrow H_1$ occurs on isobaric supply of heat, and this will probably be accompanied with volume-contraction; that on the three-phase line $G + H_1 + H_2$ the transformation $H_2 + G \rightarrow H_1$ occurs on supply of heat, and that this is certainly accompanied with volume-contraction, then we know that probably both, but certainly the line $G + H_1 + H_2$ possesses a negative value for $\dfrac{dp}{dT}$.

If we take this into account for both lines, then it will be clear that this quadruple point will present the shape of fig. 6, where the angle between $L + H_1 + H_2$ and $G + L + H_1$ does not contain metastable prolongations. I shall postpone a discussion of the further peculiarities which appear for inverse melting-points, to a later occasion.[1])
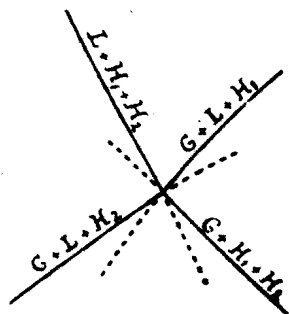

Fig. 6.

Another example, in which the rule enables us to infer easily what quadruple points are possible, we find among others for a dissociating compound in solid state by the side of the least volatile component, liquid and vapour; then we know that this quadruple point can occur on different branches of the three-phase line: compound + liquid + vapour.

Let us consider the case that the pressure continually decreases from the first to the second component; then the quadruple point can lie in the first place on the three-phase line so that neither melting-point, nor maximum sublimation point appear stable. If this is the case then the order of the phases is G L V S, in which V denotes the solid compound, S the solid second component. The angle without metastable prolongations lies therefore between $G+L+V$ and $L+V+S$, and in this the coexistences $G + L$, $L + V$ and $V + S$ occur according to the first formulation of the rule.

If, however, on the three-phase line of the compound the melting-point occurs, but the maximum sublimation point does not occur, the succession has become GVLS, so that just as in the preceding case we cannot meet with metastable prolongations in the angle between $G + V + L$ and $V + L + S$, and now find the coexistences $G + V$, $V + L$ and $L + S$ between the two lines. As is known this case is found among others when a salt-hydrate (before its transition to the anhydrous salt or to another hydrate) possesses a melting point.

If the compound has both a melting-point and a maximum point of sublimation, the order has become VGLS, and no metastable prolongation occurs in the angle between $V + G + L$ and $G + L + S$, where the coexistences $V + G$, $G + L$, and $L + S$ are found.

Led by these considerations we can easily construct the quadruple points under discussion.

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[1]) A similar type of quadruple points we find also in the system Iron-carbon. SMITS. Z. f. Elektrochemie 18. 362 (1912).

In conclusion one of the few applications of the second kind may be briefly mentioned here.

In my first communication[1] concerning the system hydrogen sulphide-water I have fully determined the situation of the quadruple point S (hydrate) by the side of two liquids (L_1 and L_2) and gas (G) with the three-phase lines terminating there. If this rule had been known to me already then, I could have directly inferred from the figure of the cited communication that between the three-phase lines $S + L_1 + G$ and $S + L_1 + L_2$ no metastable prolongations occur, that there the coexistences:

$S + L_1$ (angle $< 180°$ between $S + L_1 + G$ and $S + L_1 + L_2$)

$L_1 + G$ „ „ „ $S + L_1 + G$ and $L_1 + L_2 + G$) and

$S + L_2$ „ „ „ $S + L_2 + G$ and $S + L_1 + L_2$)

occur, and that therefore the order of the phases must be GL_1SL_2, if the mentioned coexistences are to take place between phases that are consecutive in concentration. The gas of these phases containing the greatest quantity of hydrogen sulphide, it is clear that the hydrate contains less water than L_2, and that therefore the liquid L_2 lies on the side of the water. From determinations which I carried out later on, and which I have communicated in my second paper[2] on this system it appears that this conclusion is really valid.

Anorganic Chemical Laboratory of the University.

Amsterdam, September 18, 1912.

Physics. — *"Isotherms of diatomic substances and of their binary mixtures.* XII. *The compressibility of hydrogen vapour at, and below, the boiling point."* By H. KAMERLINGH ONNES and W. J. DE HAAS. Communication N°. 127c from the Physical Laboratory at Leiden.

(Communicated in the meetings of May 25 and June 29, 1912).

§ 1. *Introduction.* To the region covered by the investigations which have been made for many years past in the Leiden laboratory upon the equation of state for hydrogen at low temperatures (for the latest paper see Comm. N°. 100a, Proc. Dec. 1907) the present Communication adds the region for hydrogen vapour lying between —252° C. and —258° C. While the lowest reduced temperature

[1] These Proc. January. 1911. p. 829.
[2] These Proc. June. 1911. p. 195.