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Chemistry. — “*In-, mono- and divariant equilibria*” II. By
Prof. F. A. H. SCHREINEMAKERS.

5. *Ternary systems.* ¹⁾

In an invariant point of a ternary system five phases occur, which we will call 1, 2, 3, 4 and 5; consequently this point is a quintuplepoint. Five curves, therefore, start from this point, which we shall call (1), (2), (3), (4) and (5) according to our former notation. Further we find $\frac{1}{2}(n+2)(n+1) = 10$ regions, viz. 123, 124, 134, 234, 125, 135, 235, 145, 245 and 345.

We call the three components of which the ternary system is composed: *A*, *B* and *C*; the five phases then can be represented by five points of the plane *ABC*. These five points may be situated with respect to one another in three ways, as has been indicated in figs. 1, 3 and 5. In fig. 1 they form the anglepoints of a quint-angle; in fig. 3 they form the quadrangle 1 2 5 3, within which the point 4 is situated; in fig. 5 they form the triangle 1 2 5, within which the points 3 and 4 are situated.

We can however consider figs. 3 and 5 also as quintangles; in each of them the sides have been drawn and the diagonals have been dotted. We call fig. 3 a monoconcave and fig. 5 a biconcave quintangle.

We are able to make of fig. 3 a monoconcave quintangle in different ways; we do this, however, in the following way. We draw in the quadrangle, within which the point 4 is situated, the diagonals 15 and 23. These divide the quadrangle into four triangles; the point 4 is situated within one of these triangles. Now we unite the anglepoints 1 and 2 of this triangle with the point 4 and we consider the lines 14 and 24 as sides of the quintangle, so that a monoconcave quintangle is formed.

In order to change fig. 5 into a quintangle we draw a straight line through the points 3 and 4; this intersects two sides of the triangle, in our case the sides 12 and 15. We now replace the side 12 by the two lines 14 and 24, the side 15 by the lines 13 and 35, so that a biconcave quintangle arises.

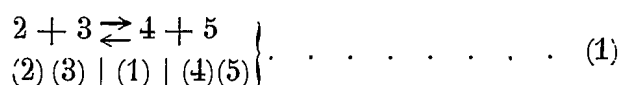
In the figs. 1, 3 and 5 the anglepoints are numbered in the following way. We take any anglepoint and we call this the point 1; two diagonals start from this point. Now we go along one of

¹⁾ For another treatment confer F. A. H. SCHREINEMAKERS. Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOM III. 218.

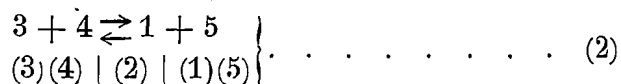
these diagonals towards another anglepoint and we call this 2, from this point we go again along a diagonal towards another anglepoint, which we shall call 3; in the same way we go from point 3 towards point 4 and from this point towards point 5. (See the figs. 1, 3 and 5). We call this order of succession "the diagonal succession". It will appear from our further considerations for what reason this definite order of succession has been chosen.

Type I. Now we shall deduce the P, T -diagram when the five phases form, as in fig. 1, the anglepoints of a convex quintangle.

As the lines 23 and 45 intersect one another, it follows for the phases of curve (1):



We find for the phases of curve (2):



Now we draw in a P, T -diagram (fig. 2) arbitrarily the curves (1) and (2); for fixing the ideas we take (2) at the left of (1). With regard to this the above mentioned reactions have been written at once in such a way that also herein curve (2) is situated at the left of (1). [For the distinction of "at the right" and "at the left" of a curve we have previously assumed that we find ourselves in the invariant point on this curve facing the stable part].

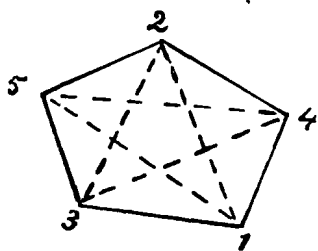


Fig. 1

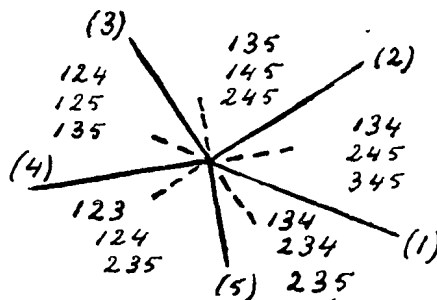


Fig. 2.

Now we shall determine the position of curve (3). It is apparent from the first reaction that the curves (2) and (3) are situated at the same side of curve (1); as (2) is situated at the left of (1), (3) must consequently be situated also at the left of (1).

It is apparent from the second reaction that (3) and (1) are situated on different sides of (2); as, according to our assumption

curve (1) is situated at the right of (2), (3) must consequently be situated at the left of (2).

Consequently we find: curve (3) is situated, at the left of (1) and of (2); curve (3) is situated therefore, as is also drawn in fig. 2, between the stable part of curve (2) and the metastable part of curve (1).

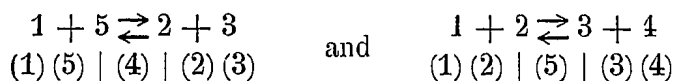
Now we determine the position of curve (4). It follows from the first reaction that (4) is situated at the right of (1); it is apparent from the second reaction that (4) is situated at the left of (2). Curve (4), therefore, as is also drawn in fig. 2, must be situated between the metastable parts of the curves (1) and (2).

At last we have still to determine the position of curve (5). It is apparent from the reactions above that curve (5) is situated at the right of (1) and of (2). Consequently curve (5) is situated within the angle, formed by the stable part of curve (1) and the metastable part of curve (2). Within this angle we also find however the metastable part of curve (3); consequently we now still have to examine in what way curve (5) is situated with respect to curve (3). We take for this the reaction between the phases of curve (3); we find from fig. 1:



As we know already that (1) and (2) are situated at the right of (3), we have written this reaction immediately in this way that also herein (1) and (2) are situated at the right of (3). From this is at once apparent that (5) must be situated at the left of (3). According to the previous it is apparent, therefore, that curve (5) must be situated between the metastable parts of the curves (2) and (3).

Besides the reactions 1, 2, and 3 we may still deduce two other reactions from fig. 1; those reactions refer to the phases of the curves (4) and (5). Although those reactions are no more wanted, they may however be used as confirmation. We find:



The partition of the curves, which follows from this is also in accordance with fig. 2.

Now we have still to deduce the partition of the regions. Between the curves (1) and (2) the region (12) = 345 extends itself, between (1) and (3) the region (13) = 245, between (1) and (4) the region (14) = 235 and between (1) and (5) the region (15) = 234. When drawing those regions we have to bear in mind that a region-angle

is always smaller than 180° . When we determine in a similar way the position of the other regions, we find a partition as in fig. 2.

The following is apparent from fig. 2. When we move, starting from a point of the curve (1), around the quintuplepoint, the succession of the curves is: (1), (2), (3), (4), (5) or the reverse order (1), (5), (4), (3), (2); we shall express this in the following way:

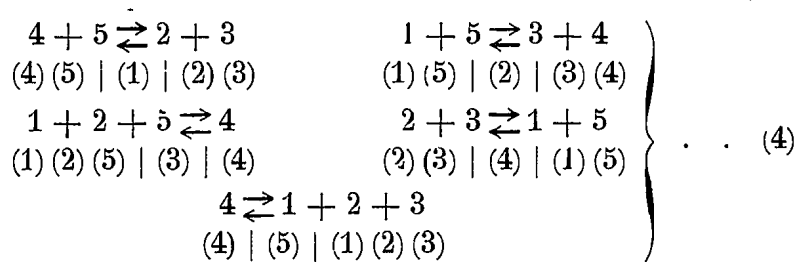
“The curves follow one another in diagonal order”.

Further it is apparent that the partition of the curves is symmetrical in that respect, that we find between every two curves the metastable part of another curve. Also we see that the regions are divided symmetrically with respect to the different curves.

This symmetrical position of curves and regions with respect to one another is based of course on fig. 1; this is viz. also symmetrical in so far that each phase is situated outside the quadrangle, which is formed by the four other phases.

Further we see in fig. 2 again the confirmation of the rule that each region which extends over the metastable or stable part of a curve (F_p) contains the phase F_p . Let us take e. g. curve (1); the region 134 extends over the stable part of this curve, the regions 124, 125 and 135 extend over the metastable part; each of these regions contains the phase 1.

Type II. Now we consider the case that the five phases form the anglepoints of a monoconcave quintangle (fig. 3). In order to determine the position of the curves (1)—(5) we take the five reactions:



Now we draw in a P, T -diagram (fig. 4) the curves (1) and (2); for fixing the ideas we take (2) at the right of (1). According to this the above-mentioned reactions, which refer to the phases of the curves (1) and (2) have been written at once in such a way that herein curve (2) is situated at the right of (1).

It follows at once from the first and the second of the reactions above, that curve (3) is situated at the right of (1) and (2). Consequently curve (3) is situated, as is also drawn in (fig. 4) within the

angle, which is formed by the stable part of curve (2) and the metastable part of curve (1).

It also follows immediately from the first and the second of the reactions above, that curve (4) is situated at the left of (1) and at the right of (2). Curve (4) is consequently situated between the metastable parts of the curves (1) and (2), and reversally the metastable part of curve (4) is situated between the stable parts of the curves (1) and (2). This is therefore drawn in fig. 4.

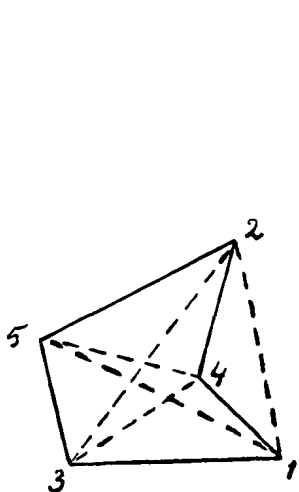


Fig. 3.

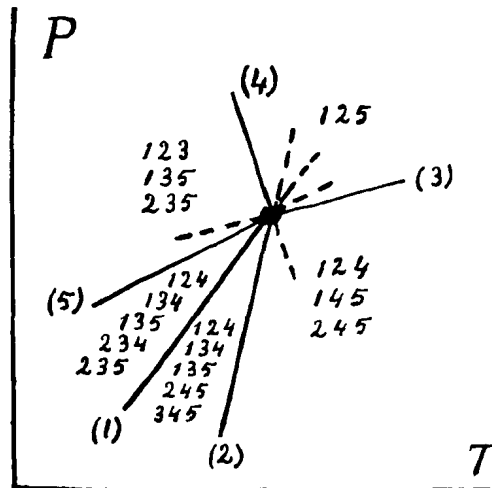


Fig 4.

It follows also from the first two reactions that curve (5) is situated at the left of (1) and (2). Consequently curve (5) is situated within the angle, which is formed by the stable part of curve (1) and the metastable part of curve (2). [Confer fig. 4]. This angle, however, is divided into two parts by the metastable part of curve (3), so that we have still to know the position of (5) and (3) with respect to one another. We can do this with the aid of the third of the reactions mentioned above; from this it appears viz. that the curves (1), (2), and (5) are situated on the same side of curve (3); curve (5) is consequently situated on the left side of (3), therefore, within the angle, which is formed by the stable part of curve (1) and the metastable part of curve (3). [Confer fig. 4].

We have used for the determination of the mutual position of the five curves, the three first reactions only; we see that the division with respect to the curves (4) and (5), which follows from the last two reactions, is also in accordance with fig. 4.

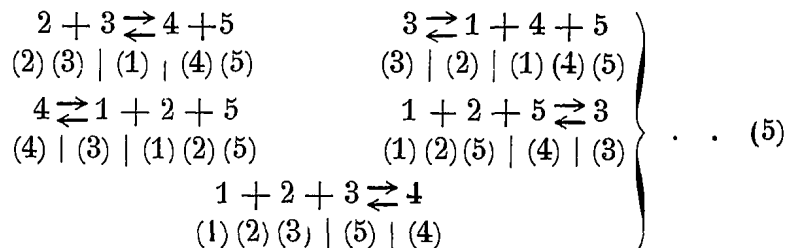
When we determine, in the way treated above, the partition of the regions, we find this as is indicated in fig. 4.

It is apparent from fig. 4 that again also in this case the curves follow one another in diagonal succession. The partition of the curves is no more symmetrical, however; between the curves (1) and (5) and between (2) and (3) no metastable curve is found; between (1) and (2) we find the metastable part of one curve [viz. of curve (4)]; between (3) and (4) and also between (4) and (5) we find two metastable curves. This is also in accordance with fig. 3; herein phase 4 has a particular position with respect to the phases 1 and 2; this is also the case in fig. 4 with curve (4) with respect to the curves (1) and (2). In fig. 3 phase 4 has also a particular position with respect to the phases 3 and 5; this is moreover the case in fig. 4 with curve (4) with respect to the curves (3) and (5).

We see also in fig. 4 the confirmation of the rule, that each region, which extends over the metastable or stable part of a curve (F_p), contains the phase F_p . When we take e.g. curve (1); the regions 124 and 134 extend themselves over the stable part of this curve; the regions 125 and 135 extend themselves over the metastable part; each of these regions contains the phase 1.

The regions 125 and 135 extend themselves over the metastable parts of the curves (1) and (5); both the regions contain the phases 1 and 5. The region 124 extends itself over the curves (1) and (2); it contains therefore the phases 1 and 2.

Type III. Now we shall yet consider the case that the five phases form the anglepoints of a biconvex quintangle (fig. 5). In order to determine the position of the five curves with respect to one another, we take the reactions:



We now draw in a P, T -diagram (fig. 6) the curves (1) and (2); we take curve (2) at the left side of (1). In connection with this we have written both the first reactions immediately in such a way that also herein (2) is situated at the left of (1).

The position of curve (3) follows also at once from both the first reactions, viz. at the left of (1) and of (2), consequently we have to draw in fig. 6 curve (3) within the angle, which is formed by the stable part of curve (2) and the metastable part of curve (1).

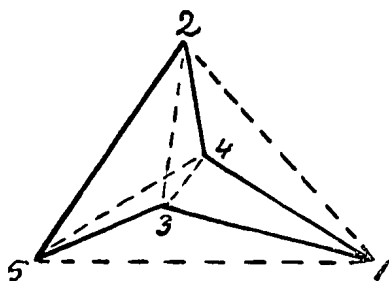


Fig. 5.

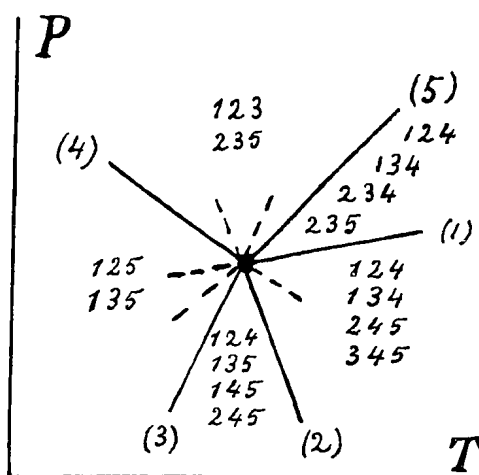


Fig. 6.

It follows also from both the first reactions that curve (4) is situated on the righthand side of (1) and of (2); consequently it is situated in fig. 6 within the angle, which is formed by the stable part of curve (1) and the metastable part of (2). Within this angle, however, also the metastable part of the curve (3) which has already been determined, is situated; consequently we have yet to examine the position of curve (4) with respect to curve (3). This follows from the third reaction; we know viz. already from the previous that (1) and (2) are situated on the righthand side of (3) [in connection with this the third reaction is written in such a way that herein (1) and (2) are situated at the righthand side of (3)], so that (4) must be situated at the left of (3). Hence it follows that (4) is situated within the angle, formed by the metastable parts of curves (2) and (3).

It follows still also from both the first reactions that curve (5) is situated at the right of (1) and of (2); consequently curve (5) must be situated within the angle which is formed by the stable part of (1) and the metastable part of (2). This angle is divided into three parts by the stable part of curve (4) and the metastable part of curve (3), so that we have still to examine within which of these parts the curve (5) is situated. This appears immediately from the third reaction, from which it is apparent that curve (5) is situated at the righthand side of (3). Consequently curve (5) must be situated within the angle, which is formed by the metastable part of curve (3) and the stable part of curve (1).

We have only used the first three reactions for the determination of the mutual position of the five curves. The partition of the curves, which follows from both the last reactions, is also in accordance with fig. 6.

When we determine, as has been indicated formerly, the partition of the regions, then we find this as is indicated in fig. 6.

It is apparent from fig. 6 that also again in this case the curves follow one another in diagonal succession. The partition of the curves is not symmetrical. The phases 2 and 5 (fig. 5) are situated in the same way with respect to 1, 3 and 4, the phases 3 and 4 with respect to 1, 2 and 5, while phase 1 has a particular position with respect to the others. This shows itself therefore in the position of the curves in fig. 6.

Also we see again in fig. 6 the confirmation of the rule, that each region which extends itself over the metastable or stable part of a curve (Fp), contains the phase Fp . The region 125 extends itself over the metastable part of curve (1), the regions 124, 134 and 135 extend themselves over the stable part; each of these regions contains the phase 1.

The metastable parts of the curves (1), (2) and (5) are situated in the region, which is limited by the curves (3) and (4); this region contains therefore the phases 1, 2 and 5.

When we combine the results, obtained above, then the following is apparent.

1. Three types of P, T -diagrams exist

a) as in fig. 2, when the five phases form the anglepoints of a convex quintangle (fig. 1);

b) as in fig. 4, when the five phases form the anglepoints of a monoconcave quintangle (fig. 3);

c) as in fig. 6, when the five phases form the anglepoints of a biconcave quintangle.

2. The three types differ from one another by the position of the metastable parts of the curves and by the partition of the regions; they are in accordance with one another in so far that the curves follow one another in diagonal succession.

In order to formulate the obtained results in another way, we shall call "a bundle" a group of curves, which follow one another, without metastable parts of curves occurring between them. Consequently in fig. 6 (5), (1) and (2) form a "bundle", which we shall call a "threecurvical" bundle, as it consists of three curves; curve (3) forms a "onecurvical" bundle, the same applies to curve (4).

In fig. 4 (1) and (5) form a "twocurvical" bundle; the same applies to (2) and (3); curve (4) forms a "onecurvical" bundle.

In fig. 2 each of the curves forms a "onecurvical" bundle. We

may express the results combined sub 1°, in the following way.

There exist three types of P, T -diagrams; the five phases form the anglepoints of:

a) a convex quintangle (fig. 1); then in the P, T -diagram the five curves form five "onecurvical" bundles (fig. 2).

b) a monoconcave quintangle (fig. 3); then in the P, T -diagram the five curves form two "twocurvical" and one "onecurvical" bundle (fig. 4).

c) a biconcave quintangle (fig. 5); then in the P, T -diagram the five curves form one "threecurvical" and two "onecurvical" bundles.

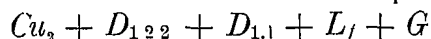
We can apply the obtained results also in the following way.

When we know the position of the five curves of a P, T -diagram, then we can easily determine to which of the types 2, 4 or 6 this diagram belongs. Hence follows at once the position of the five phases with respect to one another, viz. whether they form the anglepoints of a convex, monoconcave or biconcave quintangle.

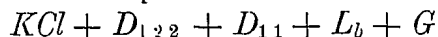
We shall discuss now an example of the partition of the curves, starting from a quintuplepoint as is found experimentally in the system: water, $CuCl_2$ and KCl . In this system occur as solid phases: KCl , $CuCl_2 \cdot 2H_2O$ and the doublesalts: $CuCl_2 \cdot 2KCl \cdot 2H_2O$ and $CuCl_2 \cdot KCl$. We use the following abbreviations: $CuCl_2 \cdot 2H_2O = Cu_2$; $CuCl_2 \cdot 2KCl \cdot 2H_2O = D_{1.2.2}$ and $CuCl_2 \cdot KCl = D_{1.1}$. We represent by G the vapour, which consists in this system of water only.

In fig. 7 the equilibria, experimentally defined, are represented; for the sake of clearness this figure is strongly schematized, otherwise it would have to be much larger e.g. the point Cu_2 is situated far too close to the point $CuCl_2$, the point $D_{1.2.2}$ far too close to the side $CuCl_2 - KCl$, etc. Yet we have taken into consideration that the different points which we have to consider, form together in fig. 7 the same quintangles as this is really the case.

At the temperature $T' = 56.1^\circ$ occurs the equilibrium:

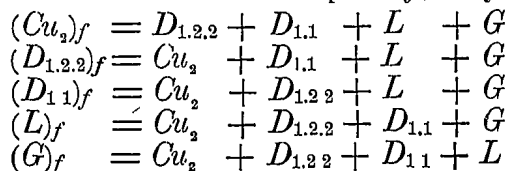


at $T_b = 93.3^\circ$ occurs the equilibrium:



As the vapour G consists of water only, in fig. 7 the points W and G coincide.

Of course five curves start from the point f , they are:



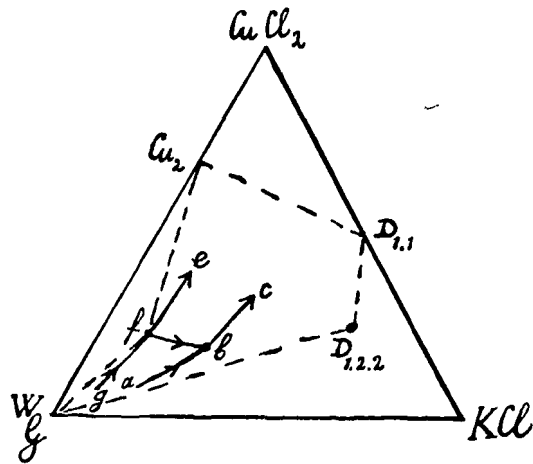


Fig. 7.

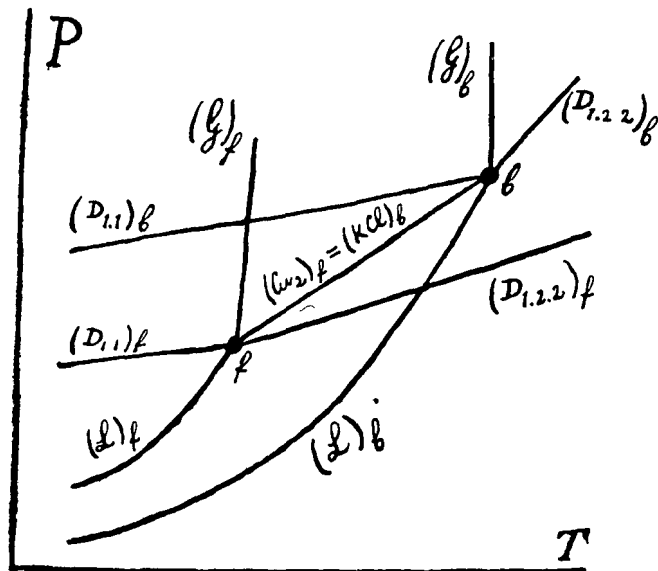


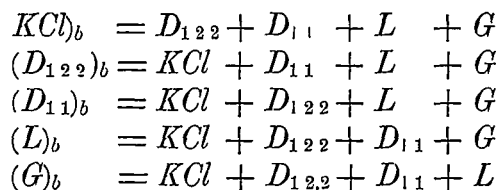
Fig. 8.

In order to indicate that these curves start from the point f , outside the parentheses the letter f is written. In fig. 7 gf represents the solutions of the equilibrium $(D_{1.1})_f$, fe those of the equilibrium $(D_{1.2.2})_f$ and fb those of the equilibrium $(Cu_2)_f$. The small arrows indicate the direction in which the temperature increases.

Also from the point b five curves start; they are:

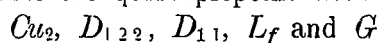
¹⁾ W. MEYERHOFFER. [Zeitschr. f. phys. Chem. 3, 336 (1889); 5, 97 (1890)] defined the compositions of the solutions of the quadruplecurves.

J. G. C. VRIENS. [Zeitschr. f. phys. Chem. 7, 194 (1891)] has measured the vapour-tensions of several points of these curves.



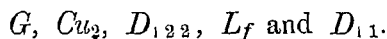
The equilibria $(Cu_2)_f$ and $(KCl)_b$ are the same, as is apparent from the occurring phases. In fig. 7 fb represents the solutions of the equilibrium $(KCl)_b$, bc represents the solutions of the equilibrium $(D_{122})_b$, and ab those of the equilibrium $(D_{11})_b$.

Fig. 8 gives a figure of the P, T -diagram, which is experimentally defined¹⁾. This is somewhat schematized for the sake of clearness. The point f represents the quintuplepoint with the phases:

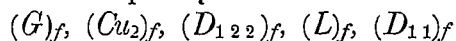


the temperature is 56.1° , the pressure is ± 73 mm. of mercury. The curves $(Cu_2)_f$, $(D_{122})_f$, $(L)_f$ and $(D_{11})_f$ starting from this point, have been defined experimentally. Curve $(G)_f$ has not been defined; it is apparent, however, that it must proceed in fig. 8 steeply onwards, a little to the right or to the left.

The five phases of the quintuplepoint form a monoconcave quintangle in fig. 7, its sides Gf , fCu_2 , $Cu_2 D_{11}$, $D_{11} D_{122}$ and $D_{122} G$ are dotted in fig. 7. [The point f therefore, corresponds with the point 4, the points G and Cu_2 with the points 1 and 2 of fig. 3]. When we take a diagonal succession of the phases, then we have, starting from G :

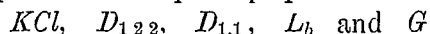


In the P, T -diagram consequently the succession



must occur, which is also found experimentally, as is apparent from fig. 8. The metastable continuations of the curves are not drawn in fig. 8; we find them by the same discussion, which has led us to fig. 4. So far as some of these metastable conditions have been realized, they are in accordance herewith.

The point b represents the quintuplepoint with the phases:



the temperature is 93.3° , the pressure ± 340 m.m. Hg . The curves, starting from this point have been defined experimentally, except curve $(G)_b$; it is apparent, however, that this must proceed in fig. 8 steeply onwards and a little to the right or to the left.

The five phases form a biconcave quintangle, the sides of which are: $W.b$, $b.D_{11}$, $D_{11} D_{122}$, $D_{122}.KCl$ and $KCl.G$ [The

¹⁾ J. G. C. VRIENS, l.c. fig. 6, p. 208.

point D_{11} , therefore, corresponds with the point 1, the points b and $D_{1.2.2}$ with the points 3 and 4 of fig. 5]. When we take a diagonal succession of the phases, then we have, starting from point G : G , $D_{1.2.2}$, L_b , KCl and D_{11} . In the P, T -diagram the succession of the curves must be, therefore:

$$(G)_b, (D_{1.2.2})_b, (L)_b, (KCl)_b, (D_{11})_b$$

As is apparent from fig. 8, this succession has been found also experimentally. We find the metastable parts of these curves (not drawn in fig. 8) by a similar discussion, as has led us to fig. 6.

(To be continued).

Crystallography. — “*On the Symmetry of the RÖNTGEN-patterns of Trigonal and Hexagonal Crystals, and on Normal and Abnormal Diffraction-Images of birefringent Crystals in general.*”
By Prof. H. HAGA and Prof. F. M. JÄGGER.

§ 1. In connection with the peculiar phenomena observed some time ago with respect to a number of RÖNTGEN-patterns of birefringent, and more especially of rhombic crystals¹⁾, we thought it necessary to investigate in a rigorously systematical way, what kind of symmetry would be found in the diffraction-patterns of uniaxial crystals, if radiated through in directions perpendicular to the optical axis. For if the supposition were right, that the suppression of the symmetry-planes expected by theory in the RÖNTGEN-patterns of rhombic crystals were connected in any way with the double refraction, — as was thought at that time by one of us, — then we might expect something of the kind also in the case of the patterns obtained by means of planeparallel sections of uniaxial crystals, if cut parallel to the optical axis, and radiated through in a direction perpendicular to that axis.

To obtain the closest analogy in the orientation with that present in the case of the rhombic crystals, which were always cut parallel to the three pinacoidal faces $\{100\}$, $\{010\}$ and $\{001\}$, we investigated in the case of tetragonal crystals those sections, which were parallel to the first and the second prisms $\{100\}$ and $\{110\}$; in the case of trigonal and hexagonal crystals we used in the same way the sections parallel to the prism-faces $\{10\bar{1}0\}$ and $\{\bar{1}2\bar{1}0\}$. In the last mentioned crystals thus the sections parallel to $\{10\bar{1}0\}$ will be analogous to those parallel to $\{100\}$ in the case of rhombic crystals, the sections parallel to $\{\bar{1}2\bar{1}0\}$ corresponding in the same way to those parallel to $\{010\}$ in the mentioned biaxial crystals.

¹⁾ These Proceedings, 17, 1204, (1915),