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Chemistry. — *"In-, mono- and divariant equilibria."*. III. By Prof. SCHREINEMAKERS.

(Communicated in the meeting of October 30, 1915).

Correction.

In the previous communication II, the figures 4 and 6, as will have been obvious to the reader, have to be changed mutually.

6. *Quaternary systems.*

In an invariant point of a quaternary system six phases occur, which we shall call A, B, C, D, E and F; consequently this point is a sextuplepoint. Six curves start from this point, therefore; in accordance with our previous notation we ought to call them (A), (B), ... (F); here, however we shall represent them by A', B', C', D', E' and F'. Further we find $\frac{1}{2}$ $(n+2)(n+1) = 15$ bivariant regions.

When we call the components K_1, K_2, K_3 and K_4 and when we represent them by the anglepoints of a regular tetrahedron, then we are able to represent each phase, which contains these four components, by a point in the space. As in a sextuplepoint six phases occur, consequently we have to consider six points in the space and their position with respect to one another.

In general this representation in space can lead to difficulties for the application to definite cases; for this reason we shall later indicate a method, which leads easily towards the purpose in every definite case. Here, however, we shall use the representation in space in order to deduce the different types of the possible P,T-diagrams.

When we consider the six points in the space, then they may be situated with respect to one another as in the figs. 1, 3, 5, and 7.

In figs. 1 and 3 they form the anglepoints of an octohedron, viz. of a solid which is limited by eight triangles. In each of these octohedrons we find twelve sides and three diagonals. [In fig. 1 AF, EC and BD are the diagonals, in fig. 3 AF, EC and EF]. In fig. 1 we find in each anglepoint four sides and one diagonal, in fig. 3 we find in the anglepoints E and F three sides and two diagonals, in the anglepoints A and C four sides and one diagonal and in the anglepoints B and D five sides only. As in fig. 1 the partition of the sides and the diagonals is a symmetrical one and, however, in fig. 3 an asymmetrical one, we shall call fig. 1 a symmetrical, fig. 3 an asymmetrical octohedron.

In fig. 5. five points form the anglepoints of a hexahedron within which the point F is situated. When we omit the side-plane BCD and when we unite F with B, C, and D, then again an octohedron arises, which we shall call monoconcave.

In fig. 7 four of the points form the anglepoints of a tetrahedron, within which the points E and F are situated. When we unite E with the points A, B and D, the point F with C, B and D, and when we omit the side-planes ABD and CBD, then a biconcave octohedron arises.

Type I. We shall deduce now the P,T-diagram, when the six phases form the anglepoints of a symmetrical octohedron (fig. 1). We may consider this solid as construed of the four tetrahedrons $CABD$, $EABD$, $FBCD$ and $FBED$, which terminate all in the side BD.

In order to determine the reaction between the phases of the monovariant equilibrium F', we consider the hexahedron $CADBE$; as the diagonal CE intersects the triangle ABD, this reaction is:

$$C + E \rightleftarrows A + B + D$$

Hence it follows:

$$C'\,E' \mid F' \mid A'\,B'\,D' \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In order to define the reaction between the phases of the monovariant equilibrium E', we take the tetrahedron $ACBDF$; as the diagonal AF intersects the triangle BCD, we find for this reaction:

$$B + C + D = A + F$$

Hence it follows:

$$B'\,C'\,D' \mid E' \mid A'\,F' \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

We now draw in a P,T-diagram (fig. 2) in any way the curves E' and F'; for fixing the ideas we draw E' at the left of F'. [For the definition of "at the left" and "at the right" of a curve we have previously assumed that we find ourselves in the invariant point on this curve, facing the stable part]. In accordance with this assumption (1) and (2) have been written also at once in such a way that herein E' is situated at the left of F'.

It now follows from (1) and (2) that C' is situated at the left of F' and E'; C' is situated, therefore, as has also been drawn in fig. 2, between the stable part of E' and the metastable part of F'.

Further it follows from (1) and (2) that the curves B' and D' are situated at the right of F' and at the left of E'; they must, therefore, as is also drawn in fig. 2, be situated between the metastable parts of the curves E' and F'. The position of B' and D'

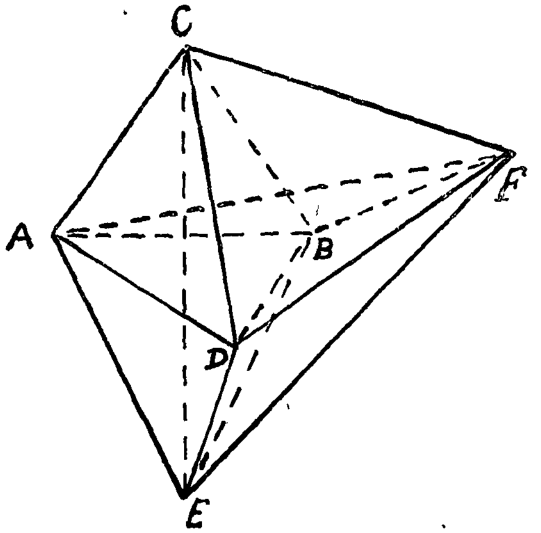

Fig. 1.

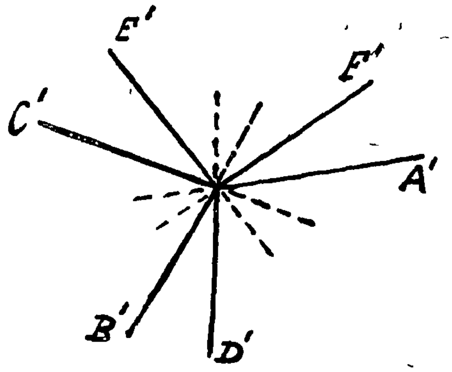

Fig. 2.

with respect to one another is, however, not yet defined, we shall refer to this later.

Further it follows from (1) and (2) that A' is situated at the right of F' and E'; consequently A' is situated within the angle, which is formed by the stable part of curve F' and the metastable part of curve E'. As however also the metastable part of curve C' is situated within this angle, we have still to define the position of A' with respect to this curve. For this we take the hexahedron $BCEFD$; as the diagonal BD intersects the triangle CEF, we find:

$$C'\,E'\,F' \mid A' \mid B'\,D' \quad \dots \dots \quad (3)$$

Hence it is apparent that C', E' and F' must be situated at the one side, B' and D' at the other side of A'; consequently A' must be situated between the stable part of F' and the metastable part of C'.

In order to define the position of A' and C' with respect to one another, we might have considered also the hexadron $DCEFB$. As the diagonal BD intersects the triangle CEF, we find:

$$B'\,D' \mid C' \mid A'\,E'\,F' \quad \dots \dots \quad (4)$$

In accordance with what has been deduced above we find here that B' and D' must be situated at the one side and A', E' and F' at the other side of curve C'.

In order to define the position of B' and D' with respect to one another, we have to know the reactions, which occur in the monovariant systems B' and D'; we shall refer to this later.

When we introduce, as in the case of ternary systems, the idea "bundle of curves", then we may express the results in the following way: when the six phases form the anglepoints of a symmetrical octahedron, then the six monovariant curves form in the P,T-diagram three "twocurvical" bundles.

Now we should yet also have to consider the bivariant regions; as, however, the reader can easily draw them in each of the P,T-diagrams, we shall omit this. Later we shall, however, refer to an example.

Type II. In fig. 3 the six phases form the anglepoints of an asymmetrical octohedron. We may consider this solid as to be composed of three tetrahedrons, which terminate in the side BD.

In order to define the position of the curves with respect to curve F', we consider the hexahedron $CADBE$, hence we find:

$$C'\,E' \mid F' \mid A'\,B'\,D' \,.\quad .\quad .\quad .\quad .\quad .\quad . \qquad (5)$$

In order to find the position of the curves with respect to curve E', we consider the hexahedron $ABDCF$; hence we deduce:

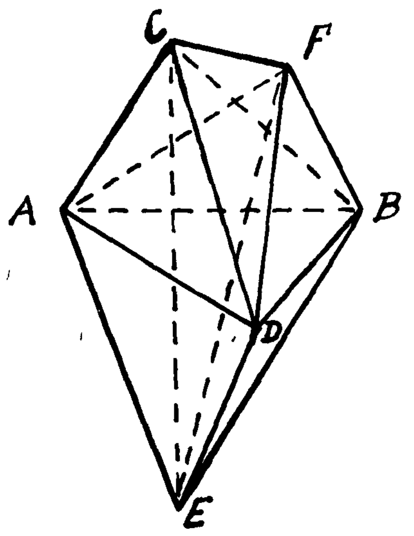

Fig. 3.

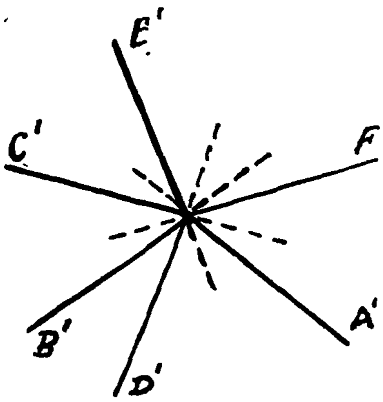

Fig. 4.

$$B'\,C'\,D' \mid E' \mid A'\,F' \,.\quad .\quad .\quad .\quad .\quad .\quad . \qquad (6)$$

Now we draw in a P,T-diagram (fig. 4) the curves E' and F' and we take in this case E' at the left of F'. For this reason (5) and (6) have been written also in such a way that herein E' is situated at the left of F'.

It follows from (5) and (6) that B' and D' are situated both at the right of F' and at the left of E'; consequently, as is also drawn in fig. 4, they must be situated between the metastable parts of E' and F'. The position of B' and D' with respect to one another is, however, not yet defined by this; we shall refer to this later.

Further it follows from (5) and (6) that C' is situated at the left of F' and E'; consequently C' is situated within the angle which is formed by the stable part of E' and the metastable part of F'.

For the position of A' it follows from (5) and (6) that A' must be situated at the right of F' and E'; consequently A' is situated in fig. 4 within the angle, which is formed by the stable part of F' and the metastable part of E'. As however this angle, is divided into two parts by the metastable part of C'', we cannot tell yet within which of those two angles we have to draw curve A'. In order to examine this, we consider the hexahedron $EBDCF$; we find from this:

$$E'F'|A'|B'C'D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence it is apparent that we must find at the one side of A' the curves E' and F', at the other side the curves B', C' and D'. Consequently it follows from this that A' must be situated between the metastable parts of the curves C' and E'.

We should have been able to find the same with the aid of the hexahedron $EABDF$; hence it follows:

$$E'F'|C'|A'B'D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now it appears from this that we must find at the one side of C' the curves E' and F', at the other side the curves A', B' and D'.

It is apparent from fig. 4 that we may express the previous results in the following way:

when the six phases form the anglepoints of an asymmetrical octohedron, then the six monovariant curves form in the P,T-diagram four onecurvical and one twocurvical bundle.

Type III. In fig. 5 the six phases form the anglepoints of the hexahedron $EABDC$, within which the point F is situated. In order to transform this hexahedron into an octohedron, we unite F with the three anglepoints of a definite side-plane of the hexahedron; we find this side-plane in the following way. In fig. 5 S represents the point of intersection of the diagonal CE with the triangle ABD. We imagine the hexahedron to be divided into six tetrahedrons, which terminate in the point S. As the point S is situated within the tetrahedron $SBDC$, we take for the side plane, mentioned above, the triangle BDC and we unite therefore the point F with the points B, C and D.

Consequently we may consider the solid as a monoconcave octohedron, which is composed of the tetrahedrons $EABD$ and $CABD$, diminished with $FBCD$; these tetrahedrons terminate again, the same as in the figs. 1 and 3 in the side BD.

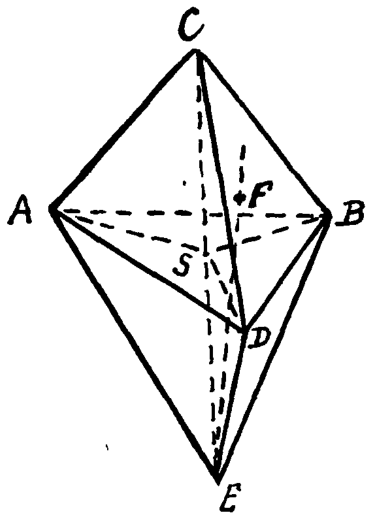

Fig. 5.

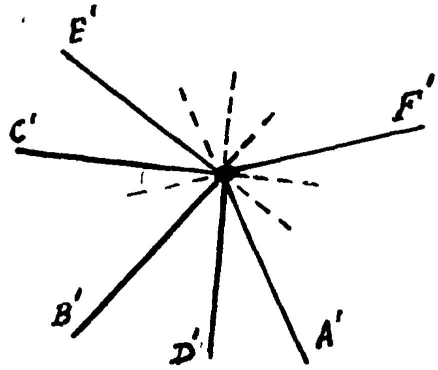

Fig. 6.

In order to define the position of the curves with respect to F' and E', we consider the hexahedron $EABDC$ and the tetrahedron $ABCD$, within which the point F is situated. We find:

$$C'E'|F'|A'B'D' \quad \ldots \ldots \quad (9)$$

$$\text{and } A'B'C'D'|E'|F' \quad \ldots \ldots \quad (10)$$

Now we draw again in a P,T-diagram the curves F' and E' (fig. 6) and we take again E' at the left of F'.

In this connection (9) and (10) have been written at once in such a way that also herein E' is at the left of F'.

It follows from (9) and (10) that C' must be situated at the left of F' and of E'; consequently C' must be situated within the angle, which is formed by the stable part of E' and the metastable part of F'.

Further it is apparent from (9) and (10) that A', B' and D' must be situated at the right of F', but at the left of E'; consequently they are situated, as is also drawn in fig. 6 within the metastable parts of E' and F'.

Now we have still to define the position of the three curves A', B' and D' with respect to one another. From the tetrahedron $CBDE$ within which the point F is situated, it follows:

$$F' \mid A' \mid B'C'D'E' \quad \ldots \ldots \quad (11)$$

so that at the one side of A' only F', at the other side B', C', D'

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and E' must be situated. Consequently curve A' is situated as is drawn in fig 6.

The contemplation of the hexahedron $EABDF$ gives us:

$$E'F' \mid C' \mid A'B'D' \quad \ldots\ldots\ldots \quad (12)$$

but it does not teach us anything new.

Now we have still to define the position of B' and D' with respect to one another, we shall refer to this later.

When we summarize the obtained results, we may say:

when the six phases form the anglepoints of a monoconcave octohedron, then the six monovariant curves form in the P, T-diagram one threecurvical, one twocurvical and one onecurvical bundle.

Type IV. In fig. 7 the six phases form the anglepoints of the tetrahedron $ABCD$, within which the points E and F are situated. The line EF intersects the triangles ABD and CBD; now we unite E with A, B and D and also F with C, B and D. Consequently we may consider the solid as a biconcave octohedron, which is composed of the tetrahedron $ABCD$, diminished with the tetrahedrons $EABD$ and $FCBD$. These three tetrahedrons terminate again in the side BD.

From the position of the five phases of the equilibrium F' with respect to one another we find:

$$E' \mid F' \mid A'B'C'D'. \quad \ldots\ldots\ldots \quad (13)$$

It follows for the position of the equilibrium E':

$$A'B'C'D' \mid E' \mid F'. \quad \ldots\ldots\ldots \quad (14)$$

Now we draw in a P,T-diagram (fig. 8) again the curves F' and E' and we take again E' at the left of F', in accordance with this also in (13) and (14) E' is taken at the left of F'.

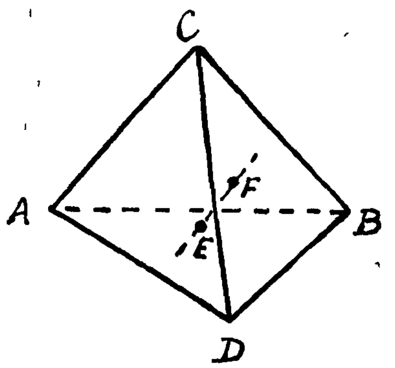

Fig. 7.

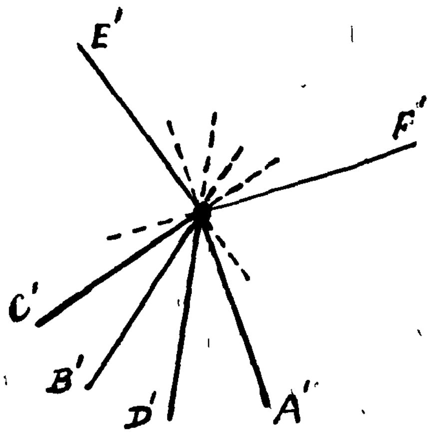

Fig. 8.

Now it follows from (13) and (14) that the bundle of the curves A', B', C' and D' must be situated at the right of F' and at the left of E'; therefore, these curves are situated, as is also drawn in fig. 8, within the angle, which is formed by the metastable parts of E' and F'.

Now we have still to define the position of those four curves with respect to one another. As the five phases of the equilibrium A' form a tetrahedron $EBCD$, within which the point F is situated, we find:

$$F' \mid A' \mid B'C'D'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Hence it follows that curve A' must be situated as is drawn in the figure.

The five phases of the equilibrium C' form the tetrahedron $FABD$, within which the point E; hence it follows:

$$E' \mid C' \mid A'B'D'F' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Hence it is apparent that curve C' must be situated as is drawn in the figure.

Later we shall define the position of the curves B' and D' with respect to one another.

We have found the following above:

when the six phases form the anglepoints of a biconcave octohedron, then the six monovariant curves form in the P,T-diagram one fourcurvical and two onecurvical bundles.

Though we have deduced the four types of the P,T-diagrams without knowing the position of the curves B' and D' with respect to one another, yet we shall define the position of the curves B' and D' with respect to one another. For this we have to consider the position of the five phases of each of the equilibria B' and D'.

For this we consider the line AF; this line intersects in each of the solids (figs. 1, 3, 5 and 7) either the triangle BCE or the triangle DCE. Now we assume that it intersects in each of these solids the triangle BCE.

As the five phases of the equilibrium D' form the hexahedron $ACEBF$, the diagonal of which intersects the triangle CEB, it follows:

$$A'F' \mid D' \mid B'C'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The five phases of the equilibrium B' form the anglepoints of the hexahedron $ACDEF$. As, in accordance with our assumption the line AF does not intersect the triangle CDE, the line CE will intersect the triangle AFD. Hence it follows:

$$A'D'F' \mid B' \mid C'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

It is apparent from (17) that in each of the figures 2, 4, 6 and

8, we must find at the one side of curve D' the curves A' and F' and at the other side the curves B', C' and E'. Therefore curve D' must be situated, as it is drawn in each of these figures. Consequently also by this the place of curve B' is defined.

We should have been able to deduce the same also from (18).

In each of the P,T-diagrams, when starting in a definite direction from B, the succession of the curves is: $B'D'A'F'E'C'$. In order to understand the meaning of this succession, we shall bear in mind the following. The points B, D, and A of the solids, are particular points, each defined in a particular way. BD is viz. the side in which terminate the tetrahedrons, of which we imagined each octohedron to be built up. On this side the point B occupies again a special place, as we have assumed that the line AF intersects the triangle BCE. Also the point A is a particular point, as the line AF intersects the triangle BCE.

When we compare the succession of the curves in the P,T-diagrams with the succession of the anglepoints of the solids then we go in these solids first along the sides from B towards D and afterwards towards A. Starting from A we go along a diagonal, consequently towards F; starting from F we go along the other diagonal, consequently towards E (figs. 3, 5 and 7) or, when no other diagonal starts from F (fig, 1) we go along a side towards the point, which is situated on the other side of the triangle ABD, consequently also towards E. At last we go, starting from E along a diagonal, consequently towards C.

When we summarize the results obtained above, the following is apparent:

1. There exist four types of P,T-diagrams. The six phases form the anglepoints of

a. a symmetrical octohedron (fig. 1); then in the P,T-diagram the six curves form three twocurvical bundles (fig. 2);

b. an asymmetrical octohedron (fig. 3); then in the P,T-diagram the six curves form one twocurvical and four onecurvical bundles (fig. 4);

c. a monoconcave octohedron (fig. 5); then in the P,T-diagram the six curves form one threecurvical, one twocurvical and one onecurvical bundle (fig. 6);

d. a biconcave octohedron (fig. 7); then in the P,T-diagram the six curves form one fourcurvical and two onecurvical bundles (fig. 8).

2. The four types are in accordance with one another in that respect that the curves succeed one another in a same definite succession. (*To be continued*).