**Chemistry**. — *"In-, mono- and divariant equilibria"*. IV. By Prof. F. A. H. SCHREINEMAKERS.

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7. Another representation of $P,T$-diagrams.

In order not to extend unnecessarily the number of drawings of $P,T$-diagrams, we shall represent these diagrams in another way. We take e. g. the $P,T$-diagram in fig. 2 (II) [1]; we shall represent this by the following figure, which we shall call a symbolical representation of this diagram.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stab. | (1) | | (5) | | (4) | | (3) | | (2) | | (1) | |
| | \| | | \| | | \| | | \| | | \| | | \| | (1) |
| | | \| | | \| | | \| | | \| | | \| | | |
| Metast. | | (3) | | (2) | | (1) | | (5) | | (4) | | |

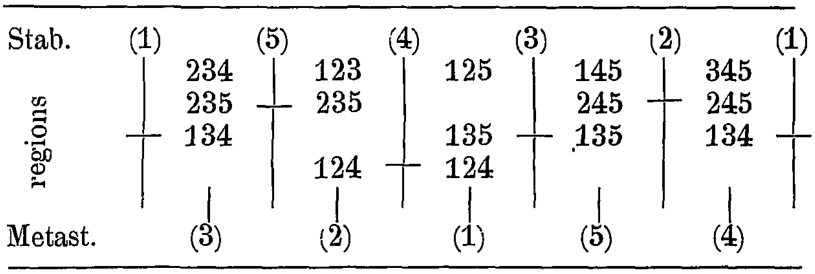
In the $P,T$-diagram [fig. 2 (II)] the stable parts of the curves succeed one another in the succession (1). (5), (4), (3), (2), (1), viz. starting from curve (1) in right-hand side direction; this succession is represented in the symbolical representation (1) by the upper line. In order to avoid errors this line is indicated by "stab."

The lower line, which is indicated by "metast." relates to the metastable parts of the curves. Consequently it is apparent from the symbolical representation, in accordance with the $P,T$-diagram [fig. 2 (II)], that between curves (1) and (5) the metastable part of curve (3) is situated; between (5) and (4) the metastable part of curve (2) etc. It is also apparent that curve (5) is situated between the metastable parts of the curves (2) and (3) etc. Curve (1) is situated between the metastable parts of the curves (3) and (4); this shows itself distinctly when we imagine the diagram (1) to be continued further towards the right.

In order to see from the diagram, which curves are situated at the right and at the left of a definite curve, for instance of curve (1), we take into consideration that the limit between at the right and at the left of curve (1) is formed by the metastable part of this curve (1). Hence we see that (5) and (4) are situated at the right, (2) and (3) at the left of (1). It is also apparent that (4) and (3) are situated at the right, (1) and (2) at the left of curve (5).

[1]) The Roman nnmerals I, II, or III between parentheses refer to communication I, II, or III.

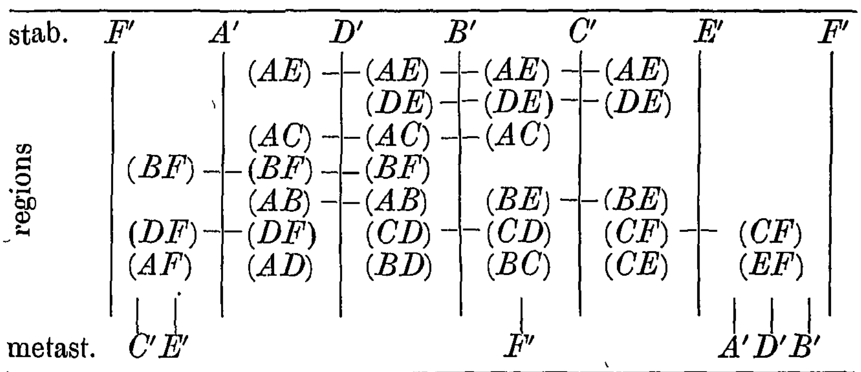
We can also include into the symbolical representation the different regions; when we do this for the previous diagram (1), then we find the diagram (2).




(2)

Hence we see that the regions 234, 235, and 134 are situated between the curves (1) and (5) and that these regions are intersected by the metastable part of curve (3); etc. The region 235 extends over curve (5), the region 124 over curve (4) etc.; this is indicated by the horizontal connecting line. It seems in diagram (2) that the region 134 consists of two parts, separated from one another. This is, however, not the case; this region extends itself viz. from curve (5) over curve (1) up to curve (2); this extension over curve (1) is indicated in the diagram also by a horizontal line.

Now we shall also replace the $P,T$-diagram of fig. 6 (III) by a symbolical representation. In fig. 6 (III) the regions are not indicated, we shall, however, include them into the symbolical representation. The same as from the $P,T$-diagram, we see from




(3)

the symbolical representation that the curves are forming three bundles, viz. one threecurvical bundle $(A'D'B')$, one twocurvical bundle $(C'E')$ and one onecurvical bundle $(F')$.

The regions are indicated in diagram (3) by placing between parentheses the two missing phases; the meaning of $(AF)$ is e. g. the region with the phases $B$, $C$, $D$, and $E$.

Altogether we find 15 regions; some of these regions extend over one or more curves; this is indicated in the diagram by horizontal connecting lines.

The same as in the $P, T$-diagram itself, we can easily deduce the position of the regions also in the symbolical representation.

We have e. g. to find the region $(AF)$ between $F'$ and $A'$; between $F'$ and $D'$ the region $(DF)$, which extends itself consequently over $A'$; between $F'$ and $B'$ the region $(BF)$ which extends itself, therefore, over the curves $A'$ and $D'$. Between $F'$ and $C'$ we find the region $(CF)$; this region $(CF)$ does not extend itself over the curves $A'$, $D'$ and $B'$, for in that case it would extend itself also over the metastable part of curve $F'$, which is not allowed; consequently it goes starting from $F'$ over curve $E'$ towards $C'$. Between $F'$ and $E'$ we find the region $(EF)$. When we act in the same way with each of the other curves, then we find a partition of the regions as in the symbolical representation (3).

In this diagram (3) we see again the confirmation of the rule that each region, which extends itself over the stable or metastable part of a curve $F'_P$, contains also the phase $F_P$. We see e. g. that the regions $(BF)$, $(DF)$ and $(AF)$ extend themselves over the metastable parts of the curves $C'$ and $E'$; each of these regions contains the phases $C$ and $E$. The regions $(BF)$ and $(DF)$ extend themselves over the stable part of curve $A'$; both the regions contain the phase $A$. The region $(AE)$ extends itself over the stable parts of the curves $D'$, $B'$ and $C'$ and over the metastable part of curve $F'$; it contains the phases $B$, $C$, $D$, and $F$; etc.

8. Systems with an arbitrary number of components.

Up to now we have applied the method for deducing the $P, T$-diagrams only on binary, ternary, and quaternary systems. We have acted in that case in the following way.

We represented the compositions of the phases, occurring in the invariant equilibrium, by points in a concentration-diagram. This concentration-diagram was a straight line for binary systems, for ternary systems a plane, for quaternary systems the space.

The points, which indicate the compositions of the phases, may be situated with respect to one another in these diagrams in different ways; we found for binary systems one position [fig. 2 (I)], for ternary systems three different positions [fig. 1, 3 and 5 (II)], for quaternary systems four different positions [figs. 1, 3, 5 and 7 (III)].

As to each of these different positions a definite $P, T$-diagram belongs, we found for binary systems one [fig. 2 (I)], for ternary systems three [figs. 2, 4 and 6 (II)] and for quaternary systems four [figs. 2, 4, 6, and 8 (III)] different types of $P,T$-diagrams.

As we can no more represent the concentration-diagram for systems with more than four components (unless in a space with more than three dimensions) we can no more apply in the same way the method which we have followed till now.

Yet we may deduce, as we shall see further, for each arbitrary system the different types of $P,T$-diagrams. Before discussing this question we shall first indicate in what way we can deduce in each definite case the corresponding $P, T$-diagram.

We consider a system of $n$ components, in the invariant point of which the $n+2$ phases $F_1 \ldots F_{n+2}$ occur. The $n+2$ monovariant curves $(F_1) \ldots (F_{n+2})$ start from this point. When the compositions of the $n+2$ phases are known, then, as we have seen in communication I, the reactions, which occur in each of the monovariant equilibria $(F_1) \ldots (F_{u+2})$ are completely defined.

We write for the reaction between the phases of the equilibrium $(F_1)$:

$$a_2F_2 + a_3F_3 + \ldots + a_{n+2}F_{n+2} = 0 \quad . \quad . \quad . \quad . \quad (4)$$

for the reaction of the equilibrium $(F_2)$:

$$b_1F_1 + b_3F_3 + \ldots + b_{n+2}F_{n+2} = 0 \quad . \quad . \quad . \quad . \quad (5)$$

for the reaction of the equilibrium $(F_3)$:

$$c_1F_1 + c_2F_2 + c_4F_4 + \ldots + c_{n+2}F_{n+2} = 0 \quad . \quad . \quad . \quad (6)$$

etc. As in all $n+2$ monovariant equilibria occur, consequently we have also $n+2$ equations of reaction.

These $n+2$ equations, however, are not independent of one another, but they are mutually dependent, viz. in this way that two of them are sufficient to define the others. When we know for instance the equations of reaction for the equilibria $(F_1)$ and $(F_2)$, then we find them for $(F_3)$, by eliminating $F_3$ from both the first. Therefore, when we eliminate $F_3$ from (4) and (5), then we find (6). In order to find the equation for the equilibrium $(F_4)$, we eliminate $F_4$ from (4) and (5); etc.

Consequently we find: when we know the equations of reaction for 2 of the $n+2$ equilibria $(F_1) \ldots (F_{n+2})$, then those for the $n$ other equilibria are also known.

We may express this also in the following way: we can represent with the aid of the $n$ other phases the composition of two of the phases of $n+2$ phases, which occur in an invariant point.

We may also say for this: in a space with $n-1$ dimensions we can represent each point with the aid of $n$ other points of this space.

We shall first apply our previous considerations to a case. treated already formerly, viz. to a ternary system. In an invariant equilibrium the phases $P$, $Q$, $R$, $S$ and $T$ occur; we call the curves starting from the invariant point $P'$, $Q'$, $R'$, $S'$ and $T'$. When the compositions of the phases are known, we can find the equations of the reactions as we have proved above. We assume that this reaction is for the phases of the equilibrium $P'$:

$$6Q = R + 2S + 3T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and for the phases of the equilibrium $Q'$:

$$9P = 2R + 3S + 4T \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It follows from (7):

$$Q' \mid P' \mid R'S'T' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

and from (8):

$$R'S'T' \mid Q' \mid P' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

We have written (7$a$) and (8$a$ in such a way that $P'$ is situated at the right of $Q'$. [Let the reader draw these and the following curves in a $P,T$-diagram in order to facilitate the matter; (9) gives a symbolical representation of the $P,T$-diagram.]

$$\begin{array}{lccccccccc} \text{Stab.} & Q' & & & & P' & & T'S'R' & & Q' \\ & | & | & | & | & | & | & | \; | \; | & | & | \\ \text{Metast.} & & T'S'R' & & Q' & & & & P' & \end{array} \qquad (9)$$

As in accordance with (7$a$) $R'$, $S'$ and $T'$ must be situated at the right of $P'$ and in accordance with (8$a$) these curves must be situated at the left of $Q'$, they are situated, therefore, between the metastable prolongation of $P'$ and $Q'$. Reversally the metastable prolongations of $R'$, $S'$ and $T'$ must be situated between $P'$ and $Q'$.

Now we have yet to define the position of the curves $R'$, $S'$ and $T'$ with respect to one another. For this we eliminate $R$ from (7) and (8); we find:

$$12Q = 9P + S + 2T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

consequently:

$$Q' \mid R' \mid P' S' T' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

Hence it is apparent that $S'$ and $T'$ must be situated at the same side of $R'$ as $P'$; consequently $R'$ must be situated as is indicated in (9). In order to find still the position of $S'$ and $T'$ with respect to one another, we eliminate $S$ from (7) and (8); we find:

$$18Q + R = 18P + T \quad \ldots \ldots \quad (11)$$

consequently:

$$Q'R'|S'|P'T' \quad \ldots \ldots \quad (11a)$$

Hence it is apparent that $S'$ must be situated between $R'$ and $T'$, so that the diagram is defined. When we eliminate $T$ from (7) and (8), we find:

$$24Q + 2R + S = 27P \quad \ldots \ldots \quad (12)$$

consequently:

$$Q'R'S'|T'|P' \quad \ldots \ldots \quad (12a)$$

which is in accordance with the position of the curves in the diagram.

Consequently we find: when the relations (7) and (8) exist between the five phases, then we obtain a $P,T$-diagram, which can be represented symbolically by (9). The curves form three bundles, viz. one threecurvical bundle $(T'S'R')$ and two onecurvical bundles, viz. the curves $P'$ and $Q'$. Consequently the diagram belongs to type III [fig. 6 (II)]; therefore, the five phases form the anglepoints of a biconcave quintangle.

Now we take as example a system of five components, so that we can represent no more the position of the phases with respect to one another, unless in a space of four dimensions. When we know however the compositions of the seven phases $P$, $Q$, $R$, $S$, $T$, $U$, and $V$, which occur in a septuplepoint, then the reactions, which can occur in the 7 monovariant systems are known. When we assume that the reaction between the phases of the equilibrium $P'$ is:

$$Q + 2R + 3S = T + U + 4V \quad \ldots \quad (13)$$

and the reaction between the phases of the equilibrium $Q'$:

$$2P + R + T = S + 2U + V \quad \ldots \quad (14)$$

We find for the reaction between the phases of the equilibrium $R'$ by elimination of $R$ from (13) and (14):

$$Q + 5S + 3U = 4P + 3T + 2V \quad \ldots \quad (15)$$

It follows for the reaction of the equilibrium $S'$ that:

$$Q + 6P + 5R + 2T = 7U + 7V \quad \ldots \quad (16)$$

for the reaction of the equilibrium $T'$ that:

$$Q + 2P + 3R + 2S = 3U + 5V \quad \ldots \quad (17)$$

for the reaction of the equilibrium $U'$ that:

$$2Q + 3R + 7S = 2P + 3T + 7V \quad . \quad . \quad . \quad . \quad (18)$$

And for the reaction of the equilibrium $V'$ that:

$$Q + 7S + 7U = 8P + 2R + 5T \quad . \quad . \quad . \quad . \quad (19)$$

It follows from those equations of reaction that:

$Q'R'S' \mid P' \mid T'U'V'$ . (13*a*) $S'U'V' \mid Q' \mid P'R'T'$ . (14*a*)
$Q'S'U' \mid R' \mid P'T'V'$ . (15*a*) $P'Q'R'T' \mid S' \mid U'V'$ . (16*a*)
$Q'P'R'S' \mid T' \mid U'V'$ . (17*a*) $Q'R'S' \mid U' \mid P'T'V'$ . (18*a*)
$Q'S'U' \mid V' \mid P'R'T'$ . . . . . . . (19*a*)

In (13*a*) and (14*a*) we have taken $P'$ at the right of $Q'$, so we shall do it also in the $P,T$-diagram. [Let the reader draw in order to facilitate the matter this and the following curve in a $P,T$-diagram; then he will see that (20) gives a symbolical representation of this]. Further it is apparent from (13*a*) and (14*a*) that $R'$ is situated at the left of $P'$ and at the right of $Q'$, consequently between $P'$ and $Q'$. It follows further from (13*a*) and (14*a*) that $S'$ is situated at the left of $P'$ and of $Q'$, consequently in the angle, formed by the stable part of $Q'$ and the metastable part of $P'$. It follows also from (13*a*) and (14*a*) that $T'$ is situated at the right of $P'$ and $Q'$, consequently within the angle formed by the stable part of $P'$ and the metastable part of $Q'$.

As however this angle is divided into two parts by the metastable part of curve $S'$, we have still to define the position of $S'$ and $T'$ with respect to one another. We see this e. g. from (16*a*) from which it is apparent that $T'$ must be situated on the same side of $S'$ as the curves $P'$, $Q'$ and $R'$. Consequently curve $T'$ is situated within the angle, formed by the stable part of $P'$ and the metastable part of $S'$.

Further it follows from (13*a*) that $U'$ and $V'$ are situated at the right of $P'$, from (14*a*) it follows that these curves are situated at the left of $Q'$, consequently $U'$ and $V'$ are situated within the angle formed by the metastable parts of $P'$ and $Q'$. However we find yet also within this angle the metastable part of curve $R'$, so that we have still to define the position of $R'$, $U'$ and $V'$ with respect to one another. We find this easily from (15*a*); hence it is apparent that $U'$ is situated on the same side of $R'$ as $Q'$ and $S'$; consequently $U'$ is situated within the angle formed by the metastable parts of the curves $R'$ and $P'$. Further it follows that $V'$ is situated on the same side of $R'$ as the curves $P'$ and $T'$, so that $V'$ must be situated between the metastable parts of $R'$ and $Q'$.

We have defined, therefore, the position of the curves in the $P,T$-diagram, although we have only used four [13*a*, 14*a*, 15*a* and

16$a$] of the seven relations. The partition of the curves, which follows from 17$a$, 18$a$ and 19$a$, is in accordance with the $P,T$-diagram.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stab. | $P'\,T'$ | | $V'$ | $U'$ | | $S'\,Q'$ | $R'$ | $P'$ | (20) |
| Metast. | | $S'\,Q'$ | | $R'$ | $P'\,T'$ | | $V'$ | $U'$ | |

It is apparent from the $P,T$-diagram or from its symbolical representation (20) that the curves form five bundles, viz. the two two-curvical bundles $(P'\,T')$ and $(S'\,Q')$ and the three onecurvical bundles $V'$, $U'$ and $R'$.

When we include also the regions in the diagram, then we find the symbolical representation (21)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stab. | $P'$ | $T'$ | $V'$ | $U'$ | $S'$ | $Q'$ | $R'$ | $P'$ |
| regions | $(ST)$ | | | | $(ST)$ | $(ST)$ | $(ST)$ | |
| | $(RV)$ | $(RV)$ | | | $(RS)$ | $(RS)$ | $(RV)$ | |
| | $(QT)$ | | $(QV)$ | $(QV)$ | $(QV)$ | $(QT)$ | $(QT)$ | |
| | $(PU)$ | $(PU)$ | $(PU)$ | $(RU)$ | $(RU)$ | $(RU)$ | | |
| | $(PV)$ | $(PV)$ | $(SV)$ | $(SV)$ | $(PS)$ | $(PS)$ | $(PS)$ | (21) |
| | $(RT)$ | $(TU)$ | $(TU)$ | $(QU)$ | $(QU)$ | | $(RT)$ | |
| | | | | | | $(PQ)$ | $(PQ)$ | |
| | $(PT)$ | $(TV)$ | $(UV)$ | $(SU)$ | $(QS)$ | $(QR)$ | $(PR)$ | |
| Metast. | | $S'\,Q'$ | $R'$ | $P'\,T'$ | | $V'$ | $U'$ | |

We find 21 regions, some of them extend themselves over one or more curves; this is indicated in the diagram by horizontal lines of conjunction. The region $(ST)$ seems in (21) to consist of two parts, separated from one another; this is however not the case, both the parts meet one another viz. over curve $P'$.

The region $(ST)$ goes therefore starting from curve $S'$ over $Q'$, $R'$ and $P'$ up to $T'$; it is apparent that it cannot go starting from $S'$ over $U'$ and $V'$ towards $T'$; viz. in this case it would cover the metastable part of curves $S'$ and $T'$, which is not allowed.

The same applies to the regions $(RV)$, $(QT)$ and $(RT)$, which consist in (21) also seemingly of two parts separated from one another. We also see again the confirmation of the rule that each region, which extends itself over a curve $F'_p$, contains the phase $F_p$.

It appears from the previous considerations: when we know the compositions of the phases, occurring in an invariant point, then we can deduce the corresponding type of the $P,T$-diagram.

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