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Chemistry. - "In-, mono- and divariant equilibria". V. By, Prof. F. A. H. Schreinemakers.
(Communicated in the meeting of December 18, 1915).
9. Another deduction of the $P, T$-diagramtypes.

Up to now we have deduced the $P, T$-dagramtypes for unary, binary, ternary and quaternary systems and we have indicated also in what way we can find the $P, T$-dagramtype for every definte system, composed of an arbitrary number of components. We have, however, supposed in all these deductions, that ether the concen' tration-dagramtype or the compositions of the phases, occurring in the invariant point, are known. Now we shall deduce, without knowing the type of the concentration-diagram or the composition of the phases, the different types of the, $P, T$-dagram, which may occur in an arbitrary system of $n$-components.

In our previous considerations we have introduced the idea "bundle of curves". A bundle of curves is formed viz. by curves, which follow one another in a $P, T$-diagram, without being separated from one another by metastable parts of curves.

In fig. 2 (I) the curves (1) and (4) form, therefore, a twocurvical bundle, the same is the case with the curves (1) and (5) and also with the curves (2) and (3) of fig. 4 (II). [We have to bear in mind that the figs. 4 (II) and 6 (II) have to be changed mutually, as is already communicated in the previous publication]. In fig. 2 (III) we find three twocurvical bundles, viz. $B^{\prime}+D^{\prime}, A^{\prime}+F^{\prime}$ and $C^{\prime}+E^{\prime}$, in fig. 4 (III) the twocurvical bundle $B^{\prime}+D^{\prime}$ and in fig. 6 (III) the twocurvical bundle $C^{\prime}+E^{\prime}$.

We find an example of a threecurvical bundle in figs. 6 (II) and 6 (III), of a fourcurrical bundle in fig. 8 (III) [viz. $A^{\prime}+D^{\prime}+B^{\prime}$ $\left.+C^{\prime}\right]$.

A bundle of curves is consequently limited at the right and at the left by one or more metastable parts of curves. As a limit we may call one single curve, which is situated between two metastable parts of curves, a "onecurvical bundle". In fig. 1 (I) and 2 (II) each curve forms, therefore, a onecurvical bundle.

Consequently we find in fig. 4 (II) two twocurvical - and one onecurvical bundle; in fig. 6 (II) one threecurvical and two onecurvical bundles, etc.

It is evident that also the metastable parts of the curves form bundles, so that we may also speak of one- and morecurvical metastable bundles.

In order to find the different types of the $P, T$-diagrams, we shall use the following theses.

- In a $P, T$-diagram always a same number of bundles is situated at the right and at the left of each bundle of curves.

In every $P, T$-diagram the number of bundles of curves is always odd and three at least.

In accordance with this property, which we shall show further, in a $P, T$-diagram occur, therefore, 3 or 5 or 7 etc. bundles of curves and diagrams with 2 or 4 or 6 bundles cannot exist.

In the cases treated up to now, we see the confirmation of these rules. In each of the figs. 1 (I), 2 (I), $\pm$ (II), 6 (II), 2 (III), 6 (III) and 8 (III) we find three bundles in each of the figs. 2 (II) and 4 (III) and in the symbolical diagram 21 (IV) we find five bundles.

We may deduce the above-mentioned rules a.o. in the following way. First it is apparent that a $P, T$-diagram with only one single bundle cannot exist; in this case viz. one region at least should exist with a region-angle, larger than $180^{\circ}$, which is not possible in accordance with our previous considerations.

Now we take in an arbitrary $P, T$-diagram a bundle of curves; we call the stable part of this bundle $a$, the metastable part $b$. Now we go from $a$ towards $b$ along a curred line which does not go through the invariant point. Starting from $a$ this curve intersects first a metastable, afterwards a stable, further again a metastable, afterwards again a stable bundle, etc. Arrived at $b$, we have consequently intersected just as many metastable bundles as stable ones. [At least 1 metastable and 1 stable bundle.] Therefore, when we find $n$ metastable bundles going from $a$ in righthandside direction towards $b$, then we find there also $n$ stable bundles. As, however, ever'y metastable bundle, which is situated at the right of $a$, is the prolongation of a stable bundle, which is situated at the left of $a$, consequently at the left of $a$ also $n$ stable bundles must be situated. Therefore we find : at the right and at the left of every bundle of curves always a same number of bundles is situated. Hence it follows immediately that the total number of curves is always odd and three at least.

Now we shall deduce the different types of $P, T$-diagrams with the aid of these properties.

1. Unary systems. (One component; three curves.)

In an unary system three curves occur, which have to be divided in accordance with our previous considerations over an odd number of bundles (three at least). This can take place only in one single way, viz. in such a way that three onecurvical bundles arise.

Consequently one single type exists only; this is represented in fig. 1 (I). We may also represent this diagram by $B_{1}+B_{1}+B_{1}$. This means that the $P, T$-diagram consists of three onecurvical bundles.
2. Binary systems. (Two components, four curves). Four curves may be divided over three bundles in one single way only, viz. in such a way that one bundle contains two curves and two bundles each one curve. We represent this by $B_{1}+B_{1}+B_{2}$ [the symbol $B_{n}$ represents a bundle which contains $n$ curves]; this means that the $P, T$-diagram consists of two onecurvical and one twocurvical bundle. Fig. 2 (I) gives a representation of this diagram.
3. Ternary systems. (Three components, five.curves).

When dividing five curves into an odd number of bundles we may distinguish two principal types, viz. a division over 5 and over 3 bundles. With a division over 5 bundles, the diagram :

$$
B_{1}+B_{1}+B_{1}+B_{1}+B_{1}
$$

arises, consequently a $P, T$-diagram with five'onecurvical bundles, as is also represented in fig. 2 (II).

With a division over 3 bundles 2 diagrams may arise, viz.:

$$
B_{1}+B_{1}+B_{3} \text { and } B_{1}+B_{2}+B_{2} .
$$

The first diagram consists of two onecurvical and one threecurvical bundle and is represented in fig. 6 (II), the second consists of one onecurvical and two twocurvical bundles and is drawn in fig. 4 (II).
4. Quaternary systems. (Four components, six curves).

When dividing the 6 curves into bundles we may also distinguish two principal types, viz. a division over 5 and over 3 bundles. With a division over 5 bundles the diagram

$$
B_{1}+B_{1}+B_{1}+B_{1}+B_{2}
$$

arises, consequently a $P, T$-diagram with one twocurvical and four onecurvical bundles. We find this drawn in fig. 4 (III).

With a division over 3 bundles the diagrams:

$$
B_{1}+B_{1}+B_{4}, \quad B_{1}+B_{2}+B_{8} \text { and } B_{2}+B_{2}+B_{2}
$$

may arise.
The first consists of one fourcurvical and two onecurvical bundles, we find this in fig. 8 (III); the second consists of one onecurvical, one twocurvical and one threecurvical bundle and is drawn in fig. 6 (III). The third consists of three twocurvical bundles and is found in fig. 2 (III).
5. Quinary systems. (Five components, seven curves).

With a division of 7 curves into an odd number of bundles we
can distinguish three principal types, viz. a division into 7,5 or 3 bundles.

With a division of 7 curves into 7 bundles, the diagram

$$
B_{1}+B_{1}+B_{1}+B_{1}+B_{1}+B_{1}+B_{1}
$$

arises, consequently a diagram with 7 onecurvical bundles. It is represented in fig. 1 by $a$.


Fig. 1.


Fig. 2.

With a division of the curves over 5 bundles the diagrams:

$$
\begin{gathered}
B_{1}+B_{1}+B_{1}+B_{1}+B_{3} \quad B_{1}+B_{1}+B_{1}+B_{2}+B_{2} \\
\text { and } B_{1}+B_{1}+B_{2}+B_{1}+B_{2} .
\end{gathered}
$$

The first of these diagrams consists of one threecurvical and four onecurvical bundles, it is represented in fig. 1 by $b$.

The second and third diagrams consist both of three onecurvical and two twocurvical bundles. These diagrams differ, however, mutually, because the bundles of curves have another position with respect to one another. The second is represented in fig. 1 by $c$ the third by $d$.

When dividing the curves over three bundles the diagrams:
$B_{1}+B_{1}+B_{5}, B_{2}+B_{2}+B_{4}, B_{1}+B_{3}+B_{3}$ and $B_{2}+B_{2}+B_{3}$. arise. The first consists of one fivecurvical and two onecurvical bundles; we find it in fig. $2 e$. The second consists of one onecurvical, one twocurvical and one fourcurvical bundle [fig. $2 f$ ]. The third consists of one onecurvical and two threecurvical bundles [fig. $2 g$ ]; the fourth consists of one threecurvical and two twocurvical bundles [fig. 2 h ].

Consequently we find that in a quinary system exist the eight types of the $P, T$-diagram, which are drawn in the figs. 1 and 2.

In the previous communication IV we have deduced the type of the $P, T$-diagram for a definite case of a system of five components. For this we found the symbolical diagram 20 (IV); this consists of three onecurvical bundles (viz. $V^{\prime}, U^{\prime}$ and $R^{\prime}$ ) and of two twocurvical bundles (riz. $P^{\prime} T^{\prime \prime}$ and $S^{\prime} Q^{\prime}$ ). We have seen above that in this case two types may be distinguished; it is apparent from the symbolical diagram that it belongs to the type: $B_{1}+B_{1}+B_{2}+$ $+B_{1}+B_{2}$; consequently it may be represented by fig. $1 d$.
6. Senary systems [six components; eight curves].

When dividing eight curves into an odd number of bundles we may distinguish again three principal types, viz. a division into 7,5 or 3 bundles. We then find the following eleven types of diagrams in which for the sake of simplification the letter $B$ is omitted.

$$
1+1+1+1+1+1+2
$$

$1+1+1+1+4,1+1+1+2+3,1+1+2+1+3$, $1+1+2+2+2,1+2+1+2+2,1+1+6,1+2+5$, $1+3+4,2+2+4,2+3+3$.

The reader can easily draw or represent symbolically these types of $P, T$-diagrams.
7. Septenary systems [seven components, nine curves]. It is evident that we may now distinguish four principal types, viz. a partition over $9,7,5$, or 3 bundles. We find the following seventeen types of diagrams.

$$
1+1+1+1+1+1+1+1+1
$$

$1+1+1+1+1+1+3,1+1+1+1+1+2+2, \quad ;$
$1+1+1+1+2+1+2,1+1+1+2+1+1+2$,
$1+1+1+1+5,1+1+1+2+4,1+1+2+1+4$,
$1+1+1+3+3,1+1+3+1+3,1+1+7,1+2+6$,
$1+3+5,1+4+4,2+2+5,2+3+4,3+3+3$.
Consequently wè find one diagram with 9 , four diagrams with 7 , five with 5 and seven with 3 bundles.

It, is evident that we may find in the same way as above also the types of $P, T$-diagrams for systems with more than seven components. After the previous deductions it is quite unnecessary to further discuss this matter.

Now we shall still briefly discuss the occurrence of symmetry in the $P, T$-diagrams. We call a diagram a symmetrical one, when all bundles contain an equal number of curres. Consequently we may distinguish different cases of symmetry, viz. with onecurvical, twocurvical, threecurvical bundles, etc.

Symmetry with onecurvical bundles is only possible as the number of bundles is always an odd one, when the $P, T$-diagram contains an odd number of curves. Consequently it can occur only in systems with an odd number of components, therefore in systems with one component [fig. 1 (I)], with three components [fig. 2 (II)], with five components [fig. 1 a], with seven components [the diagram $1+1+1+1+1+1+1]$, etc.

As the number of bundles is always an odd one, $(2 n+1)$ and three at least, symmetry with twocurvical bundles is only possible when the $P, T$-diagram contains an even number of curves $(4 n+2)$, six at least. Consequently it can occur only in systems with $4 n$ components, therefore in systems with 4 components [fig. 2 (III)], in systems with 8 components, etc.

As the number of bundles is $2 n+1$, symmetry with threecurvical bundles is only possible in diagrams of systems with $3(2 n+1)$ $2=6 n+1$ components. In a system with seven components the diagram is, therefore: $B_{8}+B_{3}+B_{3}$.

It is apparent from these considerations that symmetry is possible in every system, of which the number of curves is equal to or a multiple, of $3,5,7 \ldots(2 n+1)$. In systems, in which the number of curves is $4,8,16 \ldots 2^{n}$ therefore in systems with $2,6,14 \ldots\left(2^{n}-2\right.$ components, symmetry is never possible.- We see the confirmation of this for systems with 2 components in fig. 2 (I), for those with 6 components in the deduced types of diagrams.

In connection with the deduction of the types of the $P, T$-diagram discussed above, of course the question arises: the $P, T$-diagram-types deduced above, may they all really exist; or in other words: is it possible to find for every $P, T$-diagram-type of a system of $n$-components, really $n+2$ phases of such a composition that they lead to that $P, T$-diagram? We can also put in short this question in this way: does a definite type of concentration-diagram belong to each of the $P, T$-diagram-types, deduced in the way treated above? We may show that this is the case indicating in which way we can find with each given $P, T$-diagramtype a corresponding concentrationdiagram.


Fig. 3.

For this we take fig. 3; this represents a $P, T$-diagram of $n+2$ curves, which are divided over different bundles $(A),(B),(C) \ldots$ Although in this figure all bundles, except $(A)$ and ( $R$ ) are drawn onecurvical, yet we assume in our considerations that they are all morecurvical. We call the curves of bundle ( $A$ ), going from the left towards the right $\left(A_{1}\right),\left(A_{2}\right),\left(A_{3}\right) \ldots$; those of bundle ( $B$ ), also going from the left towards the right $\left(B_{1}\right),\left(B_{2}\right), \ldots$; the same applies to the curves of the other bundles. We call the $n+2$ phases occurring in the invariant point: $A_{1}, A_{2}, A_{3} \ldots B_{1}, B_{2} \ldots C_{1}, C_{2} \ldots$ etc.

Now we shall deduce the reactions, which may occur between those phases. Previously we have seen that they are completely defined, when we know two equations of reaction. In order to determine these reactions, we start from the reactions which answer the 'position of the curves with respect to curves $\left(A_{1}\right)$ and $\left(R_{1}\right)$; we call those curves the position-curves. [Of course we may choose for this every two arbitrary curves].

We find from fig. 3 for the reaction of the phases with respect to curve $\left(A_{1}\right)$ :

$$
\left.\begin{array}{c}
r_{1} R_{1}+r_{2} R_{2}+\ldots+s_{1} S_{1}+s_{2} S_{2}+\ldots+t_{1} T_{1}+t_{2} T_{2}+\ldots= \\
a_{2} A_{2}+a_{3} A_{3}+. .+b_{1} B_{1}+b_{2} B_{2}+\ldots+c_{1} C_{1}+c_{2} C_{2}+\ldots+d_{1} D_{1}+d_{2} D_{2}+. . \tag{1}
\end{array}\right\}
$$

in which the reaction-coefficients $r_{1} r_{2} \ldots$ etc. are however unknown, but they are all positive. The sum of the reaction-coefficients at the right and at the left of the sign of equation must be the same. We find from fig. 3 for the reaction of the phases with respect to curve ( $R_{1}$ );

$$
\left.\begin{array}{c}
\left.r_{2}^{\prime} R_{2}+r_{3}^{\prime} R_{3}+\ldots+s_{1}^{\prime} S_{1}+s_{2}^{\prime} S_{2}+\ldots+t_{1}^{\prime} T_{1}+t_{2}^{\prime} T_{2}+\cdots\right) \\
+a_{1}^{\prime} A_{1}+a_{2}^{\prime} A_{2}+\ldots=b_{1}^{\prime} B_{1}+b_{2}^{\prime} B_{2}+\ldots  \tag{2}\\
c_{1}^{\prime} C_{1}+c_{2}^{\prime} C_{2}+\ldots+d_{1} D_{1}+d_{2}^{\prime} D_{2}+\ldots
\end{array}\right\}
$$

in which the reaction-coefficients are still also unknown, but they are all positive. Also again the sum of the reaction-coefficients at the right and at the left of the sign of equation must be the same. We multiply (1) by $\lambda$ and deduct (2) therefrom ; we find:

$$
\left.\begin{array}{c}
\lambda r_{1} R_{1}+\left(\lambda r_{2}-r_{2}^{\prime}\right) R_{2}+\ldots+\left(\lambda s_{1}-s_{1}^{\prime}\right) S_{1}+\left(\lambda s_{2}-s_{2}^{\prime}\right) S_{2}+\cdots \\
+\left(\lambda t_{1}-t_{1}^{\prime}\right) T_{1}+\left(\lambda t_{2}-t_{2}^{\prime}\right) T_{2}+\ldots==1 \\
a_{1}^{\prime} A_{1}+\left(\lambda a_{2}+a_{2}^{\prime}\right) A_{3}+\left(\lambda a_{3}+a_{3}^{\prime}\right) A_{3}+\ldots+\left(\lambda b_{1}-b_{1}^{\prime}\right) B_{1}+  \tag{3}\\
\left(\lambda b_{2}-b_{2}^{\prime}\right) B_{2}+\ldots+\left(\lambda c_{1}-c_{1}^{\prime}\right) C_{1}+\left(\lambda c_{2}-c_{2}^{\prime}\right) C_{2}+\cdots \\
+\left(\lambda d_{1}-d_{2}^{\prime}\right) D_{1}+\left(\lambda d_{2}-d_{2}^{\prime}\right) D_{2}+\ldots
\end{array}\right\} .
$$

In this equation (3) the coefficient $a^{\prime}{ }_{1}$ of the phase $A_{1}$ is always positive.

In order to find from (3) the reaction with respect e.g. to curve $\left(C_{\mathrm{I}}\right)$, we put:

$$
\begin{equation*}
\lambda c_{1}-c_{1}^{\prime}=0 \text { consequently } \lambda=\frac{c_{1}^{\prime}}{c_{1}} \tag{4}
\end{equation*}
$$

Hence we find some conditions, which the reaction-coefficients in (1) and (2) must satisfy. It is apparent viz. from fig. 3 that all the curves of the bundles $(T),(A)$ and $(B)$ are situated on the same side of curve ( $C_{1}$ ) as curve $\left(A_{1}\right)$. As in (3) the coefficient of $A_{1}$ is positive, the coefficients of $A_{2}, A_{8}, \ldots$ and $B_{1}, B_{2} \ldots$ in (3) must be also positive and those of the phases $T_{1}, T_{2}, \ldots$ negative. The first condition, viz. that the coefficients of $A_{2}, A_{3}, \ldots$ are positive, is satisfied; we write the two other conditions:

$$
\begin{equation*}
\lambda>\frac{b_{1}^{\prime}}{b_{1}}, \lambda>\frac{b_{2}^{\prime}}{b_{2}}, \lambda>\frac{b_{3}^{\prime}}{b_{3}} \text { etc. } \lambda<\frac{t_{1}^{\prime}}{t_{1}}, \lambda<\frac{t^{\prime}}{t_{2}} \text { etc. } \tag{5}
\end{equation*}
$$

in which 2 has the value, indicated in (4).
Further it is apparent from fig. 3 that the curves $\left(C_{2}\right),\left(C_{3}\right), \ldots$ and the bundles.$D),(R)$ and $(S)$ are situated on the other side of curve ( $C_{1}$ ) as curve ( $A_{1}$ ). Hence it follows that in (3) the coefficients
of the phases $C_{2}, C_{3} \ldots$ and $D_{1}, D_{2} \ldots$ are negative, those of the phasès $R_{1}, R_{2} \ldots$ and $S_{1}, S_{2} \ldots$ must be positive. Consequently we find:

$$
\begin{align*}
& \lambda<\frac{c_{2}^{\prime}}{c_{2}}, \lambda<\frac{c_{3}^{\prime}}{c_{3}} \text { etc. } \lambda<\frac{d_{1}^{\prime}}{d_{1}}, \lambda<\frac{d_{2}^{\prime}}{d_{2}} \text { etc. } \\
& \lambda>\frac{r_{2}^{\prime}}{r_{2}}, \lambda>\frac{r_{3}^{\prime}}{r_{3}} \text { etc. } \lambda>\frac{s_{1}^{\prime}}{s_{1}}, \lambda>\frac{s_{2}^{\prime}}{s_{2}} \text { etc. } \tag{6}
\end{align*}
$$

wherein 2 has again the value, indicated in (4). Consequently we find the following: when the curves must be situated with respect to curve $\left(C_{1}\right)$ as is assumed in fig. 3, then the coefficients of the reaction-equations (1) and (2) must satisfy the conditions (5) and (6).

Let us take still another example. In order to find from (3) the reaction with respect to e.g. curve $\left(D_{3}\right)$ we put:

$$
\begin{equation*}
\therefore \quad \wedge d_{3}-d_{3}^{\prime}=0 \text { consequently } \lambda=\frac{d^{\prime} s}{d_{3}} \tag{7}
\end{equation*}
$$

In fig. 3 the curves $\left(D_{1}\right)$ and $\left(D_{2}\right)$ and the bundles $(A),(B)$ and $(C)$ are situated on the same side of curve $\left(D_{3}\right)$ as curve $\left(A_{1}\right)$. The coefficients of the phases $D_{1}$ and $D_{2}$, those of $A_{1}, A_{2} \ldots, B_{1}, B_{2} \ldots$ and $C_{1}, C_{2} \ldots$ in (3) must, therefore, all be positive. Hence it follows:

$$
\begin{gather*}
\lambda>\frac{d_{1}^{\prime}}{d_{1}} \quad \lambda>\frac{d_{2}^{\prime}}{d_{2}}  \tag{8}\\
\lambda>\frac{b_{1}^{\prime}}{b_{1}}, \quad \lambda>\frac{b_{2}^{\prime}}{b_{2}} \text { etc. } \lambda>\frac{c_{1}^{\prime}}{c_{1}}, \quad \lambda>\frac{c_{2}^{\prime}}{c_{2}} \text { etc. }
\end{gather*}
$$

wherein $\lambda$ has the value, indicated in (7).

- Further it follows from fig. 3 that the curves $\left(D_{4}\right),\left(D_{6}\right) \ldots$ and the bundles $(R),(S)$ and $(T)$ are situated on the other side of curve $\left(D_{3}\right)$ as curve $\left(A_{1}\right)$. The coefficients in (3) of the phases $D_{4}, D_{5} \ldots$ must, therefore, be negative, those of the phases $R_{1}, R_{2} \ldots, S_{1}, S_{2} \ldots$ and $T_{1}, T_{2} \ldots$ must, therefore, be positive. Hence it follows:

$$
\begin{align*}
& \lambda<\frac{d_{4}^{\prime}}{d_{4}}, \quad \lambda<\frac{d_{5}^{\prime}}{d_{5}} \text { etc. } \quad \lambda>\frac{r_{3}^{\prime}}{r_{2}}, \quad \lambda>\frac{r_{3}^{\prime}}{r_{3}} \text { etc. }  \tag{9}\\
& \lambda>\frac{s_{1}^{\prime}}{s_{1}}, \quad \lambda>\frac{s_{3}^{\prime}}{s_{2}} \text { etc. } \quad \lambda>\frac{t_{1}^{\prime}}{t_{1}}, \quad \lambda>\frac{t_{2}^{\prime}}{t_{2}} \text { etc. }
\end{align*}
$$

wherein $\lambda$ has again the value, indicated in (7).
Consequently we find: when the curves must be situated with respect to curve ( $D_{\mathrm{s}}$ ) as is assumed in fig. 3, then the coefficients 'of the reaction-equations (1) and (2) must satisfy the conditions 8). and (9).

We could áet in the same way for each of the curves of fig. 3; then we find all conditions which must be satisfied by the coefficients from (1) and (2). It follows, however, rather soon from a comparison of fig. 3 with the reaction-equation (3) that the conditions are:

$$
\begin{equation*}
\frac{a_{3}^{\prime}}{a_{2}}>\frac{a_{3}^{\prime}}{a_{3}}>\frac{a_{4}^{\prime}}{a_{4}}>\ldots \tag{10}
\end{equation*}
$$

and

$$
\left.\begin{array}{c}
\left.\frac{r_{2}^{\prime}}{r_{2}}<\frac{r_{3}^{\prime}}{r_{3}}<\cdots<\frac{b_{1}^{\prime}}{b_{1}}<\frac{b_{2}^{\prime}}{b_{2}}<\ldots<\frac{s_{1}^{\prime}}{s_{1}}<\frac{s_{2}^{\prime}}{s_{2}} \ldots<\right)  \tag{11}\\
<\frac{c_{1}^{\prime}}{c_{1}}<\frac{c_{3}^{\prime}}{c_{2}}<\ldots<\frac{t_{1}^{\prime}}{t_{1}}<\frac{t_{2}^{\prime}}{t_{2}}<\cdots<\frac{d_{1}^{\prime}}{d_{1}}<\frac{d_{2}^{\prime}}{d_{3}}<\cdots
\end{array}\right\}
$$

The reader will easily find a regularity in these conditions (10) and (11) in connection with fig. 3. In (11) we find viz. first the coefficients, relating to the phases of bundle ( $R$ ), afterwards to the phases of bundle $(B)$, then to those of bundle $(S)$, further to those of bundle ( $C$ ), etc. and for each bundle in the same order, in which the curves in that bundle succeed one another from left to right.

In these conditions the reaction-coefficients $a_{1}^{\prime}$ and $r_{1}$ of the phases $A_{1}$ and $R_{1}$ do not occur; this is based on the fact that we have taken the curves $\left(A_{1}\right)$ and ( $R_{1}$ ) as position-curves.

Now the question arises whether we can always find reactioncoefficients, satisfying

$$
\begin{gather*}
r_{1}+r_{2}+\ldots s_{2}+s_{2}+\ldots+t_{1}+t_{2}+\ldots= \\
=a_{2}+a_{8}+\ldots+b_{1}+b_{2}+\ldots+c_{1}+c_{2}+\ldots+d_{1}+d_{2} \ldots  \tag{12}\\
r_{2}^{\prime}+r_{8}^{\prime}+\ldots+s_{1}^{\prime}+s_{2}^{\prime}+\ldots+t_{1}^{\prime}+t_{3}^{\prime}+\ldots+a_{1}^{\prime}+a_{2}^{\prime}+\ldots=  \tag{13}\\
=b_{1}^{\prime}+b_{2}^{\prime}+\ldots+c_{1}^{\prime}+c_{2}^{\prime}+\ldots+d_{1}^{\prime}+d_{2}^{\prime}+\ldots
\end{gather*}
$$

and also (10) and (11). It is evident that this is always the case and that we can find large series of values for those coefficients.

When we take definite values for the coefficients in (1) and (2), then the question arises whether the compositions of the phases are defined by this. We see, however, at once that this is not at all the case and that those compositions may strll change within very large limits. With each type of the $P, T$-diagram consequently infinitely many concentration-diagrams correspond, which are, however, all bound to the same limiting conditions $\lfloor 10,11,12$, and 13] and. they form, therefore, a definite type of concentrationdiagram.

When we take a ternary system, it appears easily that the compositions of the phases are not perfectly defined, even if we assume definite values for the reaction-equations:

Let us take e.g. the reaction-equation:

$$
a A+b B=c C+d D .
$$

Hence it is only apparent that the four phases form the anglepoints of a convex quadrangle, the point of intersection of the diagonals divides the diagonal $A B$ into parts, which bear to one another the relation $a: b$ and the diagonal $C D$ into parts which bear to one another the relation as $c: d$. Hence it is not only apparent that intinitely many quadrangles exist, but also that the place of those quadrangles in the flat plane is still quite arbitrary.

Consequently we are allowed to conclude from the previous considerations:
the $P, T$-diagramtypes, deduced above, can all exist; with each of the $P, T$-diagramtypes corresponds a definite type of the concen-tration-diagram, which may be deduced in the way indicated above.

Herewith, of course, the question is not solved whether in the experimental examination of all systems e.g. with 5 components, all eight $P, T$-diagramtypes possible (fig. 1 and 2) will occur. For this it is necessary that the phases really occurring, lead to the eight possible types of the concentration-diagram and only the experiment can decide that.

Now we shall apply the previous considerations, in order to find with some $P, T$-diagramtypes a corresponding concentrationdiagramtype. The types of concentrationdiagrams, belonging to the $P, T$ diagramtypes of the binary, ternary and quaternary systems have already been discussed before (I, II and III). As these concentrationdiagramtypes were represented graphically, we have followed there the reverse way, viz. we have deduced from these types the corresponding $P, T$-diagramtypes.

We take for , an example a system with 5 components, in the invariant point of which the seven phases $A, B, C, D, E, F$, and $G$ occur; we assume that the $P, T$-diagram consists of 7 onecurvical bundles, as in fig. $1 a$. We choose the curves $(\Lambda)$ and $(E)$ as positioncurves. The reactions are:

$$
\begin{aligned}
& e E+f F+g G=b B+c C+d D \\
& f^{\prime} F+g^{\prime} G+a^{\prime} A=b^{\prime} B+c^{\prime} C+d^{\prime} D
\end{aligned}
$$

The reaction-coefficients must satisfy:

$$
\begin{gather*}
e+f+g=b+c+d  \tag{14}\\
f^{\prime}+g^{\prime}+a^{\prime}=b^{\prime}+c^{\prime}+d^{\prime} . \tag{15}
\end{gather*}
$$

and also the conditions (10) and (11). It is evident that (10) disappears and that (11) passes into:

$$
\begin{equation*}
\frac{b^{\prime}}{b}<\frac{f^{\prime}}{f}<\frac{c^{\prime}}{c}<\frac{g^{\prime}}{g}<\frac{d^{\prime}}{d} . \tag{16}
\end{equation*}
$$

by which the concentrationdiagram-type is defined. When we wish a definite example, we may take among others:

$$
\begin{aligned}
& 2 E+F+3 G=4 B+C+D \\
& F+9 G+A=2 B+2 C+7 D
\end{aligned}
$$

wherein the coefficients satisfy (14), (15) and (16).
Now we take a system with 5 components, in the invariant point of which the phases $P, Q, R, S, T, U$, and $V$ occur; we take fig. $1 d$ for the type of the $P, T$-diagram.

When we take $(R)$ and $(U)$ as position-curves, the equations of the reactions are:

$$
\begin{aligned}
& u U+s S+q Q=p P+t T+v V \\
& s^{\prime} S+q^{\prime} Q+r^{\prime} R=p^{\prime} P+t^{\prime} T+v^{\prime} V .
\end{aligned}
$$

De reaction-coefficients have to satisfy:

$$
u+s+q=p+t+v \quad, \quad s^{\prime}+q^{\prime}+r^{\prime}=p^{\prime}+t^{\prime}+v^{\prime}
$$

and

$$
\frac{p^{\prime}}{p}<\frac{t^{\prime}}{t}<\frac{s^{\prime}}{s}<\frac{q^{\prime}}{q}<\frac{v^{\prime}}{v}
$$

by which the type of the concentration-diagram is defined. We may take among others as a definite example:

$$
\begin{aligned}
& 3 U+5 S+Q=4 P+3 T+2 V \\
& 7 S+2 Q+3 R=2 P+3 T+7 V
\end{aligned}
$$

These are viz. the reaction-equations (15) and (18) which we have used in communication IV for the deduction of fig. $1 d$ [symbolically represented in communication IV by (20) and (21)].

As third example we take a system with 5 components, in the invariant point of which the phases $A, B, C, D, E, F$, and $G$ occur, for the type of the $P, T$-diagram we take fig. $2 g$. We take $(A)$ and $(E)$ as position-curves, so that the equations of the reactions are:

$$
\begin{aligned}
& e E+f F+g G=b B+c C+d D . \\
& f^{\prime} F+g^{\prime} G+a^{\prime} A+b^{\prime} B+c^{\prime} C=d^{\prime} D .
\end{aligned}
$$

The reaction-coefficients have to satisfy:

$$
\begin{gathered}
e+f+g=b+c+d \quad, \quad f^{\prime}+g^{\prime}+a^{\prime}+b^{\prime}+c^{\prime}=d^{\prime} \\
\frac{b^{\prime}}{b}>\frac{c^{\prime}}{c} \quad \text { and } \quad \frac{f^{\prime}}{f}<\frac{g^{\prime}}{g}<\frac{d^{\prime}}{d}
\end{gathered}
$$

by which the type of the concentration-diagram is defined.
We may take among others as a definite example:

$$
\begin{aligned}
& 2 E+3 F+2 G=B+2 C+4 D \\
& 3 F+8 G+3 A+4 B+2 C=20 D
\end{aligned}
$$

The reader may also easily apply these considerations to other types of the $P, T$-diagram.

Leiden, Anorg. Chem. Lab. (To be continued).

