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

(Communicated in the meeting of January 29, 1916).

10. *Relation between concentration- and P,T-diagrams.*

We have seen in our previous contemplations in what way can be deduced the types of the P,T-diagram which may occur in a system of n-components and in what way the concentration-diagram belonging to each of those can be found. Now we shall consider more in detail the correspondence between the two diagrams.

Instead of 2 reactions, each between $n+1$ phases, we consider 2 reactions between the $n+2$ phases of the invariant point. We write these reactions:

$$a_1F_1 + a_2F_2 + \,..\, + a_{n+2}\,F_{n+2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$b_1F_1 + b_2F_2 + \ldots + b_{n+2}\,F_{n+2} = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We take a_1 and b_1 always positive, so that in each of these reactions one of the other coefficients at least must be negative. Further we suppose that we have written the phases $F_1\,F_2 \ldots$ in (1) and (2) in such order of succession, that:

$$\frac{b_1}{a_1} > \frac{b_2}{a_2} > \frac{b_3}{a_3} > \,..\, > \frac{b_{n+2}}{a_{n+2}}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These ratios may all be positive; when one of the ratios e.g. $b_p : a_p$ is negative, then in (3) going from left to right also all following ratios are negative. When we multiply (1) with λ and when we subtract (2) from it, then we may write:

$$a_1\left(\lambda - \frac{b_1}{a_1}\right)F_1 + a_2\left(\lambda - \frac{b_2}{a_2}\right)F_2 + a_3\left(\lambda - \frac{b_3}{a_3}\right)F_3 + \ldots = 0. \quad (4)$$

Hence we may deduce $n+2$ reaction-equations, each between $n+1$ phases. When we put $\lambda = b_1 : a_1$ then the coefficient of F_1 becomes zero; it is apparent from (4) that the coefficients $F_2, F_3 \ldots$ have the same sign as $a_2, a_3 \ldots$ We represent this by the series:

$$0 + a_2 + a_3 + a_4 \ldots + a_{n+2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When we equate $\lambda = b_2 : a_2$ then the coefficient of F_1 has the opposite sign of a_1, those of $F_3, F_4 \ldots$ obtain the same sign as $a_3, a_4 \ldots$ We represent this by the series:

$$-a_1\;0 + a_3 + a_4 \ldots + a_{n+2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For $\lambda = b_3 : a_3$ we obtain the series:

$$-a_1 - a_2\;0 + a_4 \ldots a_{n+2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and at last for $\lambda = b_{n+2} : a_{n+2}$

$$- a_1 \quad - a_2 \quad - a_3 \quad - a_4 \qquad - a_{n+1} \quad 0 \quad . \quad . \quad . \quad . \quad (8)$$

It is apparent from those series that the removal of the 0 from left to right causes a regular change of the signs.

Now we have $n + 2$ reaction-equations, so that we can easily find the type of the P,T-diagram. It is evident that this type shall depend on the signs of $a_2\, a_3 \ldots$ (a_1 is viz. positive); we could think now that those signs can be quite arbitrary, we can show however, that this is not the case for the sake of (2) and (3).

Let us imagine that the signs of $a_1\, a_2 \ldots$ are represented by the series:

$$+ + + - - + + - + - + + + + \; . \; . \; . \; . \quad (9)$$

This means that $a_1\, a_2\, a_3$ are positive, a_4 and a_5 negative, a_6 and a_7 positive, etc. We shall call a group of n equal signs following one another: an n-group; as case of limit n can also be $=1$. Consequently we find in (9) firstly a positive 3-group, afterwards a negative 2 group etc. As a_1 is taken positive, the first group therefore must always be positive.

Now we can show: "each series consists of three groups, at least".

It is apparent, without more, that the occurrence of one single group only is not possible. The impossibility of two groups occurring appears in the following way.

When we put in (3) $b_1 : a_1 = \mu_1$, $b_2 : a_2 = \mu_2$ etc. then it follows from (1) and (2):

$$a_1 + a_2 + \ldots + a_p + a_{p+1} + \ldots + a_{n+2} = 0 \; . \quad . \quad . \quad (11)$$

and

$$\mu_1\, a_1 + \mu_2\, a_2 + \ldots + \mu_p\, a_p + \mu_{p+1}\, a_{p+1} + \ldots + \mu_{n+2}\, a_{n+2} = 0 \quad (12)$$

in which

$$\mu_1 > \mu_2 > \ldots > \mu_p > \ldots > \mu_{n+2} \; . \quad . \quad . \quad . \quad . \quad (13)$$

We take herein $a_1 \ldots a_p$ positive and $a_{p+1} \ldots a_{n+2}$ negative; as regards the signs of $\mu_1\, \mu_2$, we take $\mu_1 \ldots \mu_q$ positive and $\mu_{q+1} \ldots \mu_{n+2}$ negative; in this q may change from 1 towards $n+2$.

Let us take $q = n + 2$; this means that all values in (13) are positive. As $a_{p+1} \ldots a_{n+2}$ are negative, we replace them by $- a_{p+1}$, $- a_{p+2}$ etc. Now (11) and (12) pass into:

$$a_1 + a_2 + \ldots + a_p = a_{p+1} + \ldots + a_{n+2} \; . \quad . \quad . \quad . \quad (14)$$

and

$$\mu_1\, a_1 + \mu_2\, a_2 + \ldots + \mu_p\, a_p = \mu_{p+1}\, a_{p+1} + \ldots + \mu_{n+2}\, a_{n+2} \; . \; (15)$$

The first side of (15) is smaller than $\mu_1 (a_1 + a_2 + \ldots + a_p)$ and larger than $\mu_p (a_1 + a_2 + \ldots + a_p)$; consequently we may write for this:

$$\alpha\, (a_1 + a_2 + \ldots + a_p) \text{ in which } \mu_1 > \alpha > \mu_p.$$

We write for the second part of (15):

$$\beta\, (a_{p+1} + \ldots + a_{n+2}) \text{ in which } \mu_{p+1} > \beta > \mu_{n+2}.$$

Consequently (15) passes into:

$$\alpha\,(a_1 + a_2 + \dots + a_p) = \beta\,(a_{p+1} + \dots + a_{n+2}) \; . \quad . \quad . \quad (16)$$

in which $\alpha > \beta$.

As neither α, nor β, nor the reaction-coefficients may be $= 0$, (11) and (12) can, therefore not be satisfied.

When we give another value to q, then we come to the same conclusion. Hence it follows, therefore, that the occurrence of two groups is not possible. As further we may easily prove that three and more groups may occur indeed, we may consequently conclude: "each series consists of three or more groups".

Now we take in (1) for $a_1\, a_2 \dots$ the series:

$$\begin{array}{c|c|c|c|c|c|c} A & R & B & S & C & T & D \\ + \dots & - \dots & + \dots & - \dots & + \dots & - \dots & + \dots \end{array} \quad . \quad . \quad (17)$$

This series consists of four positive groups, which are indicated by A, B, C, and D and of three negative groups, which are indicated by R, S and T; for the sake of clearness these groups are separated from one another by vertical lines. Going from the left to the right, we number in each group the curves: 1, 2, ..., consequently $A_1 A_2 \dots$, $B_1 B_2 \dots$

When we deduce from (1) and (2) with the aid of (4) the $n+2$ reaction equations, then we find the series:

$$\begin{array}{l|l|l|l|l|l|l} 0 + + \dots & - \dots & + \dots & - \dots & + \dots & - \dots & + \dots \\ - 0 + \dots & - \dots & + \dots & - \dots & + \dots & - \dots & + \dots \\ - - 0 \dots & - \dots & + \dots & - \dots & + \dots & - \dots & + \dots \end{array}$$

and at last:

$$- - - \dots | + \dots | - \dots | + \dots | - \dots | + \dots | - \dots 0$$

These series represent the signs of the coefficients of the reactions, which may occur each time between $n+1$ phases; they indicate, however also which curves are situated at the one and at the other side of the curve, which is represented by 0; the curves with the positive sign are situated viz. at the one side, those with the negative sign at the other side of the curve 0.

Now we find easily that the P,T diagramtype can be represented by fig. 3 (V) and that with each group of signs in (17) a bundle in the P,T diagram corresponds, which contains just as many curves as the group contains signs. We shall refer to this later.

We have assumed in series (17) an odd number of groups, when we add another negative one, then arises the series:

$$\begin{array}{c|c|c|c|c|c|c|c} A & R & B & S & C & T & D & U \\ + \dots & - \dots & + \dots & \dots & + \dots & - \dots & + \dots & - \dots \end{array} \quad . \quad (18)$$

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Hence we deduce the type of the P,T diagram in the way indicated above. Although there are in series (18) eight groups of signs, yet in the diagram not 8, but only 7 bundles are found. We obtain viz. again fig. 3 (V), in which we have, however, still to draw the curves $U_1 U_2 \ldots$ and in such a way that they form with $A_1 A_2 \ldots$ one single bundle only, in which the order of succession from left to right is $U_1 U_2 \ldots A_1 A_2 \ldots$. Consequently we find a diagram, satisfying also the series:

$$\begin{array}{c|c|c|c|c|c|c} U\ A & R & B & S & C & T & D \\ + \ldots & - \ldots & + \ldots & - \ldots & + \ldots & - \ldots & + \ldots \end{array} \quad . \ . \ (19)$$

Hence it is apparent: when the last group of a series is negative (series 18) then we may place this last group, after reversing its sign, before the first group and unite them to one single group (series 19)..

[Below we shall indicate in another way that a similar removal is possible and in what way we can carry it out.]

From the previous considerations follow at once the rules:

in each P,T diagram the number of bundles of curves is always odd and three at least;

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

We can also find in this way the types of the P,T diagram, which may occur in a system of n components. We have viz. to examine in how many and in what ways the $n+2$ signs of a series can be divided into an odd number of groups. This is perfectly the same as the way followed in communication V viz. examining in how many and in what ways $n+2$ curves can be divided into an odd number of bundles.

The following is apparent for the relation between the type of the concentration- and the P,T-diagram.

1. We know 2 reactions between the phases, which occur in the invariant point and we seek the corresponding type of the P,T-diagram. We write then those two reactions just as the equations (1) and (2) viz. in such a way that condition (3) is satisfied. Now we take the series of the signs of reaction (1); when the last group is negative, then we combine it with the first in the way indicated above (compare series 18 and 19). We may use the following properties for drawing the type of the P,T-diagram.

With each group of the series a bundle of curves corresponds, which contains as many curves as the group contains signs.

These bundles succeed one another in the same order as the groups in the series, on condition that we follow it from left to right and when we take firstly consecutively the positive groups and then the negative ones [consequently in series 18 the order of succession: $ABCDRSTU$, this is in accordance with fig. 3 (V)].

We can also take the order of succession of the groups, without taking the sign into consideration [consequently in series 18 the order of succession: $ARBS$...] Then we consider in the P,T-diagram not only the stable —, but also the metastable parts of the bundles [Consequently in fig. 3 (V) the order of succession of the bundles is $ARBS$....] Now we may say: in the P,T-diagram the bundles succeed one another in the same order as the groups in the series; the positive groups indicate the stable parts, the negative ones the metastable parts of the bundles.

In each of the bundles the curves succeed one another as in the corresponding group of the series.

2. We know the type of the P,T-diagram and we seek the corresponding type of the concentration-diagram, therefore, two reaction-equations between the phases.

For this we firstly define the series of signs, which corresponds with the P,T-diagram; this is easily found after the above considerations. As by this only the signs of the coefficients of (1) are given, we may satisfy this reaction, therefore, in infinitely many ways. Equation (2) is also still to be chosen quite arbitrarily, on condition that (3) only is satisfied. Consequently we find an infinite number of solutions, which satisfy all, however, the same conditions and which form together the type of the concentration-diagram. Consequently the type depends on the series of signs, so that we may consider the series of signs as a representation of the type of the concentration-diagram and of the P,T-diagram.

We shall refer with an example to this deduction of the type of the concentration diagram.

We shall apply those general considerations to some definite cases. We have taken in communication IV as an example (reactions 13 and 14) of 2 reactions in a septuplepoint:

$$Q + 2R + 3S = T + U + 4V \quad \ldots\ldots \quad (20)$$

and

$$2P + R + T = S + 2U + V \quad \ldots\ldots \quad (21)$$

and we have found for the corresponding type of the P,T-diagram the symbolical diagram 20 (IV) or fig. $1d$ (V). We shall deduce this diagram following the method indicated above. As in both the equations (20) and (21) one phase is missing, we are not allowed to apply to it without more our previous considerations; for this reason we shall deduce from (20) and (21) two other equations, which contain each the seven phases. We may obtain infinitely many of those equations, which are however of course dependent on (20) and (21). When we multiply e.g. (20) by 2 and when (21) is added to this then we find:

$$2P + 2Q + 5R + 5S - T - 4U - 9V = 0 \quad . \quad . \quad . \qquad (22)$$

When we multiply (20) by 3 and when we add (21) to this, then we find:

$$2P + 3Q + 7R + 8S - 2T - 5U - 13V = 0 \quad . \quad . \qquad (23)$$

Now we have to choose in (22) and (23) the order of succession of the phases in such a way that condition (3) is satisfied.

As:

$$\frac{2}{1} > \frac{8}{5} > \frac{3}{2} > \frac{13}{9} > \frac{7}{5} > \frac{5}{4} > \frac{2}{2}$$

we must consequently write (22) in the form:

$$T - 5S - 2Q + 9V - 5R + 4U - 2P = 0 \quad . \quad . \qquad (24)$$

Therefore we obtain the series of signs:

$$\begin{array}{c|cc|c|c|c|c} T & S & Q & V & R & U & P \\ + & - & - & + & - & + & - \end{array}$$

for which we can also write:

$$\begin{array}{cc|cc|c|c|c} P & T & S & Q & V & R & U \\ + & + & - & - & + & - & + \end{array} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

Hence it appears consequently that the P,T-diagram consists of the 2 twocurvical bundles $(P + T)$ and $(S + Q)$ and of the 3 onecurvical bundles (V), (R) and (U). Starting from (P) is, therefore, in accordance with (25) the order of succession of the curves: (P), (T), (V), (U), (S), (Q) and (R), which is in accordance with the symbolical diagram 20 (IV) and fig. 1d (V).

We assume that in a system with 5 components the reactions:

$$P - 2Q + R - S + T + U - V = 0 \quad . \quad . \quad . \quad . \qquad (26)$$

and

$$2P + 2Q - 4R + 2S + T - 6U + 3V = 0 \quad . \quad . \qquad (27)$$

occur. We have to choose in those equations the order of succession of the phases in such a way that condition (3) is satisfied. As

$$\frac{2}{1} > \frac{1}{1} > -\frac{2}{2} > -\frac{2}{1} > -\frac{3}{1} > -\frac{4}{1} > -\frac{6}{1}$$

we have to write, therefore, for 26:

$$P + T - 2Q - S - V + R + U = 0 \quad . \quad . \quad . \quad . \qquad (28)$$

we obtain consequently the series of signs:

$$\begin{array}{cc|ccc|cc} P & T & Q & S & V & R & U \\ + & + & - & - & - & + & + \end{array} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

The P,T diagram consists, therefore, of two twocurvical and one threecurvical bundle and it can be represented by fig. 2 h (V).

Now we shall seek the concentration-diagram belonging to a P,T diagram. We take fig. 1 a (V); as each bundle is onecurvical, the series of signs becomes:

$$\begin{array}{c|c|c|c|c|c|c} A & E & B & F & C & G & D \\ + & - & + & - & + & - & + \end{array} \quad \ldots\ldots\ldots \quad (30)$$

so that the type of the concentration diagram is defined. We can find it in the following way. From (30) follows the reaction:

$$a\,A - e\,E + b\,B - f\,F + c\,C - g\,G + d\,D = 0 \quad . \; . \quad (31)$$

wherein $a, e, b, \ldots$ are positive. We write for the second reaction:

$$a'\,A + e'\,E + b'\,B + f'\,F + c'\,C + g'\,G + d'\,D = 0 \quad . \quad (32)$$

wherein the coefficients may have positive and negative values. Now we have the conditions:

$$a - e + b - f + c - g + d = 0$$

$$a' + e' + b' + f' + c' + g' + d' = 0$$

and $$\frac{a'}{a} > -\frac{e'}{e} > \frac{b'}{b} > -\frac{f'}{f} > \frac{c'}{c} > -\frac{g'}{g} > \frac{d'}{d}$$

by which the type of the concentration-diagram is defined. It is evident that those conditions can be satisfied in infinitely many ways. We may take as example amongst others:

$$A - 2\,E + B - F + C - G + D = 0$$

and $$6A - 7\,E + 3\,B + F - 2\,C + 3\,G - 4\,D = 0$$

Herein is viz.:

$$6 > \tfrac{7}{2} > 3 > -1 > -2 > -3 > -4.$$

Below the corresponding series of signs follow for each of the P,T diagramtypes in quinary systems [figs. 1, (V) and 2 (V)]

fig. 1 a (V) $+ - + - + - +$ . . . . (33)
fig. 1 b (V) $+ + + - + - +$ . . . . (34)
fig. 1 c (V) $+ - - + - + +$ . . . . (35)
fig. 1 d (V) $+ - + + - - +$ . . . . (36)
fig. 2 e (V) $+ - + + + + +$ . . . . (37)
fig. 2 f (V) $+ - - + + + +$ . . . . (38)
fig. 2 g (V) $+ - - - + + +$ . . . . (39)
fig. 2 h (V) $+ + - - + + +$ . . . . (40)

Series 33 contains seven, each of the series 34, 35 and 36 contains five and each of the series 37, 38, 39 and 40 contains three groups of signs.

The reader himself can now easily deduce the series of signs for systems with 6 and more components.

Above we have deduced: when the last group of a series is negative, then we may place this last group, after reversion of its sign, before the first group and combine them to one single group. We have deduced this by indicating that from both the series (18 and 19) the same P,T diagram-type results.

Now we shall indicate that both series may be converted mutually and in what way this can take place.

We write reaction (1) when we put $n+2=r$ for the sake of abbreviation

$$a_1 F_1 + a_2 F_2 \dots + a_{x-1} F_{x-1} + a_x F_x + \dots + a_r F_r = 0 \quad . \quad (41)$$

we assume that a_{x-1} is positive, and that $a_x \dots a_r$ are negative, so that those last form a separate negative group, just as group U in (18). We represent the ratios by $\mu_1 \dots \mu_r$, so that

$$\mu_1 > \mu_2 > \dots > \mu_{x-1} > \mu_x > \dots > \mu_r$$

is satisfied. Reaction (2) now passes into:

$$\mu_1 a_1 F_1 + \mu_2 a_2 F_2 + \dots + \mu_{x-1} a_{x-1} F_{x-1} + \mu_x a_x F_x + \dots + \mu_r a_r F_r = 0 \quad (42)$$

It follows from (41) and (42)

$$(\mu_1-\varkappa)a_1 F_1 + \dots + (\mu_{x-1}-\varkappa)a_{x-1} F_{x-1} + (\mu_x-\varkappa)a_x F_x + \dots + (\mu_r-\varkappa)a_r F_r = 0 \quad (43)$$

wherein $\varkappa$ is arbitrary. We choose $\varkappa$ in such a way that

$$\mu_1 > \dots > \mu_{x-1} > \varkappa > \mu_x > \dots > \mu_r \quad . \quad . \quad . \quad . \quad (44)$$

is satisfied.

The negative coeff. of $F_x \dots F_r$ from (41) become positive in (43); the coefficients of $F_1 \dots F_{x-1}$ keep all the same sign. We place the positive group $F_x \dots F_r$ at the beginning of the series; then we obtain

$$(\mu_x-\varkappa)a_x F_x + \dots + (\mu_r-\varkappa)a_r F_r + (\mu_1-\varkappa)a_1 F_1 + \dots + (\mu_{x-1}-\varkappa)a_{x-1} F_{x-1} = 0 \quad (45)$$

wherein the coefficient of the first term is positive [viz. $\mu_x - \varkappa < 0$ and $a_x < 0$]. Now we take $\mu_x > 0$, so that also $\varkappa > 0$. We write for (42):

$$-\mu_x a_x F_x - \dots - \mu_r a_r F_r - \mu_1 a_1 F_1 - \dots - \mu_{x-1} a_{x-1} F_{x-1} = 0 \quad (46)$$

so that also herein the first term is positive [viz. $\mu_x > 0$ and $a_x < 0$]. Now we shall show that condition (3) is satisfied. We write this:

$$\lambda_x > \dots > \lambda_r > \lambda_1 > \dots > \lambda_{x-1} \cdot \quad . \quad . \quad . \quad . \quad (47)$$

wherein:

$$\frac{-\mu_s}{\mu_s-\varkappa} = \lambda_s \quad [s = 1, 2 \dots x \dots r].$$

Now we have:

$$\lambda_p - \lambda_q = \frac{-\mu_p}{\mu_p-\varkappa} - \frac{-\mu_q}{\mu_q-\varkappa} = \frac{\varkappa(\mu_p-\mu_q)}{(\mu_p-\varkappa)(\mu_q-\varkappa)} \quad . \quad . \quad . \quad (48)$$

When we apply (48) every time for two values of λ_p and λ_q which succeed one another, consequently for λ_1 and λ_2, for λ_2 and λ_3, etc. and also for λ_1 en λ_r, then we find when we take (44) into consideration

$\lambda_1 > \lambda_2 > \ldots > \lambda_{x-1}$; $\lambda_{x-1} < \lambda_x$; $\lambda_x > \ldots > \lambda_r$ and $\lambda_1 < \lambda_r$
so that (47) is satisfied.

When we take $\mu_x < 0$, then we write for (46) in order to make the first term positive [viz. $\mu_x < 0$ and $a_x < 0$] :

$$\mu_x a_x F_x + \ldots + \mu_r a_r F_r + \mu_1 a_1 F_1 + \ldots + \mu_{x-1} a_{x-1} F_{x-1} = 0 \qquad (49)$$

Consequently we equate now :

$$\frac{\mu_s}{\mu_s - \varkappa} = \lambda_s \, .$$

Now we have :

$$\lambda_p - \lambda_q = \frac{\mu_p}{\mu_p - \varkappa} - \frac{\mu_q}{\mu_q - \varkappa} = - \frac{\varkappa(\mu_p - \mu_q)}{(\mu_p - \varkappa)(\mu_q - \varkappa)} \quad . \quad . \qquad (50)$$

As μ_x is taken negative, $\varkappa$ can be in accordance with (44) as well positive as negative; we now give to $\varkappa$ one of the many negative values, which satisfy (44). With the aid of (44) and (50) we then find that again (47) is satisfied.

Consequently we find : when the last group of a series is negative, then we may place this, after reversing its sign, before the first one and combine them to one single group; also it is apparent in what way we can find the new coefficients.

We can still put the question whether all pairs of reaction-equations, which we can deduce from (1) and (2) will have the same series of signs. As a P,T-diagramtype is perfectly defined by its series of signs and reversally the series of signs is perfectly defined by a P,T-diagram, consequently this must be the case. When we deduce, therefore, from (1) and (2) another pair of reaction-equations, then the series of signs for this latter pair must, therefore, be the same as that for the first. Let the series of signs of the reactions (1) and (2) be given by (17), then this is also valid for each other pair of reaction-equations which can be deduced from (1) and (2). Of course it is possible that this new series of signs begins with another group; the order of succession, however, remains the same. In (17) the series begins with group A; when a new series begins e.g. with the group S, then is the order of succession :

S	C	T	D	A	R	B
$+\ldots$	$-\ldots$	$+\ldots$	$-\ldots$	$+\ldots$	$-\ldots$	$+\ldots$

or

S	B	R	A	D	T	C
$+\ldots$	$-\ldots$	$+\ldots$	$-\ldots$	$+\ldots$	$-\ldots$	$+\ldots$

In the first series the signs of the groups S, C, T, and T are the reverse of those from (17), in the second series this is the case with the groups A, R, B and S. Both the series are, however, the same as in (17); when we go in fig. 3 (V), starting from bundle A towards the right, then series (17) follows; when we go, however, starting from S towards the right or the left, then the above series follow.

We can also deduce this property without using the P,T-diagram. For this we form from (41) and (42) the two new reaction-equations:

$$(\mu_1 - \varkappa)\, a_1 F_1 + \ldots + (\mu_y - \varkappa)\, a_y F_y + \ldots + (\mu_r - \varkappa)\, a_r F_r = 0 \quad (50^a)$$

$$(\mu_1 - l)\, a_1 F_1 + \ldots + (\mu_y - l)\, a_y F_y + \ldots + (\mu_r - l)\, a_r F_r = 0 \quad (50^b)$$

wherein we give arbitrary values to l and $\varkappa$. As we are allowed to always take the last group in (41) positive, we suppose $a_r > 0$. We distinguish three principal cases.

$I^0.\ \mu_r > \varkappa \qquad II^0.\ \varkappa > \mu_1 \qquad III^0.\ \mu_1 > \varkappa > \mu_r.$

Principal case I. We may distinguish three cases:

$a.$ $\mu_1 > l$ and $l > \varkappa$; $b.$ $\mu_1 > l$ and $l < \varkappa$; $c.$ $l > \mu_1$ therefore $l > \varkappa$.

Now we can show that the equations (50^a) and (50^b) satisfy condition (3), if we take them in the given or in opposite order of succession as it appears necessary. [The reader, to whom we leave this deduction, has to bear in mind that the coefficient of the first term must be positive in both equations; in the case c this term is negative in (50^b), so that we have to reverse all signs of (50^b)].

As all signs of (50^a) are the same as in (41) the series of signs of (50^a) is, therefore, the same as that of (41).

Principal case II. We distinguish three cases:

$a)$ $l > \mu_1$, and $l > \varkappa$; $b)$ $l > \mu_1$ and $l < \varkappa$; $c)$ $l < \mu_1$ therefore $l < \varkappa$.

It appears that the series of signs of (50^a) is the same as that in (41).

Principal case III. $\mu_1 > \varkappa > \mu_r$.

We take $\varkappa$ between the two ratios μ_{y-1} and μ_y which succeed one another, so that is satisfied:

$$\mu_1 > \ldots > \mu_x > \ldots > \mu_{y-1} > \varkappa > \mu_y > \ldots > \mu_z \ldots > \mu_r.$$

We assume that in (41) the phases $F_x \ldots F_y \ldots F_z$ belong to the same series of signs; $a_x \ldots a_y \ldots a_z$ are, therefore, all either positive or negative. We write (50_a) and (50_b) in the order of succession:

$$\left.\begin{array}{l}(\varkappa-\mu_y)a_yF_y + \ldots (\varkappa-\mu_z)a_zF_z + \ldots (\varkappa-\mu_r)a_rF_r + \ldots \\ \ldots (\varkappa-\mu_1)a_1F_1 + \ldots (\varkappa-\mu_x)a_xF_x + \ldots (\varkappa-\mu_{y-1})a_{y-1}F_{y-1} = 0\end{array}\right\} . \quad (50^c)$$

$$\left.\begin{array}{l}(l-\mu_y)a_yF_y + \ldots (l-\mu_z)a_zF_z + \ldots (l-\mu_r)a_rF_r + \ldots \\ \ldots (l-\mu_1)a_1F_1 \ldots (l-\mu_x)a_xF_x + \ldots (l-\mu_{y-1})a_{y-1}F_{y-1} = 0\end{array}\right\} . \quad (50^d)$$

We distinguish again three cases viz.:

$a)$ $l > \mu_y$ and $l > \varkappa$; $b)$ $\lambda > \mu_y$ and $l < \varkappa$; $c)$ $l < \mu_y$ therefore $l < \varkappa$.

When we take care that in all those cases the coefficient of the first term is positive, then we can show that the two reaction-equations, taken in the given or in opposite order, satisfy condition (3).

Considering the signs of the phases in (41) and in (50^c), then it is apparent that the phases form in (50^c) the same groups as in (41); only the group $F_x \ldots F_y \ldots F_z$ makes an exception; this is viz. separated into two groups, of which the one viz. $F_y \ldots F_z$ is found at the beginning and the other viz. $F_x \ldots F_{y-1}$ at the end of (50^c). As both those groups have, however, an opposite sign, we can again unite them to one group. Consequently we find in (41) and in (50^c) the same groups and with respect to one another in such an order of succession, that the series of signs of (41) and that of (50^c) are the same.

We could put the question why in all considerations the series of signs of the reaction-equation:

$$a_1 F_1 + \ldots + a_{p-1} F_{p-1} + a_p F_p + \ldots + a_{n+2} F_{n+2} = 0 \quad . \quad (50^e)$$

is used and not that of the equation:

$$\mu_1 a_1 F_1 + \cdot \quad + \mu_{p-1} a_{p-1} F_{p-1} + \mu_p a_p F_p + \cdot\cdot + \mu_{n+2} a_{n+2} F_{n+2} = 0 \; (50^f)$$

We might just as well have used this, for both the reaction-equations have the same series of signs. In order to find the series of signs of (50^f), we must give another order of succession to the phases, viz. in such a way that condition (3) is satisfied. Now the ratios are, however, no more:

$$\mu_1 \, \mu_2 \ldots \mu_{n+2} \quad \text{but} \quad \frac{1}{\mu_1}, \frac{1}{\mu_2}, \ldots \frac{1}{\mu_{n+2}}.$$

When we take $\mu_1 \ldots \mu_{p-1}$ positive and $\mu_p \ldots \mu_{n+2}$ negative, then we find:

$$\frac{1}{\mu_{p-1}} > \ldots > \frac{1}{\mu_1} > \frac{1}{\mu_{n+2}} > \ldots > \frac{1}{\mu_p}.$$

Hence it is apparent, therefore, that we have to write the reaction-equations:

$$\mu_{p-1} a_{p-1} F_{p-1} + \cdot \; \cdot + \mu_1 a_1 F_1 + \mu_{n+2} a_{n+2} F_{n+2} + \ldots + \mu_p a_p F_p = 0 \; (50^g)$$

$$a_{p-1} F_{p-1} + \ldots + a_1 F_1 + a_{n+2} F_{n+2} + \ldots + a_p F_p = 0 \quad . \quad (50^h)$$

When a_{p-1} is negative, then we give the opposite sign to all phases. Considering the signs of the phases in (50^e) and (50^g) then it appears that both equations contain the same groups, so that both have the same series of signs.

It is apparent from our considerations that with each concentration-diagramtype corresponds a P,T-diagramtype and reversally and that each series of signs is a representation of both diagrams. Consequently a certain relation must exist between the two diagrams; we shall show: a P,T-diagramtype can be considered as a schematical reaction-diagramtype of the corresponding concentration-diagramtype; and reversally a concentration-diagramtype can be considered as a schematical representation of the corresponding P,T-diagramtype.

When we take e. g. the P,T-diagramtype of fig. 2 (II). Hence it is apparent that the curves (1) and (2) are situated at the one side, curves (3) and (4) at the other side of curve (5). We may express this by

$$(1)\,(2)\,|(5)|\,(3)\,(4) \quad \ldots\ldots\ldots \quad (51)$$

This relation (51) expresses however also, that in the monovariant equilibrium $(5) = 1 + 2 + 3 + 4$ a reaction occurs of the form:

$$1 + 2 \rightleftarrows 3 + 4 \quad \ldots\ldots\ldots \quad (52)$$

This reaction expresses that a complex of the phases 1 and 2 can pass into a complex of the phases 3 and 4 and reversally, the quantitative proceeding of this reaction, however, does not show itself in (52). We may deduce this quantitative proceeding from the concentration-diagram [fig. 1 (II)]; herein it is determined by the ratio of the parts into which the diagonals 12 and 34 divide one another. As 52 represents the proceeding of the reaction schematically only, we shall call for this reason 52 a schematical reaction.

Now it is evident in what way we can contemplate a P,T-diagram as a schematical reactiondiagram. For this we first change the meaning of the curves; in the P,T-diagram a curve, e. g. curve (F_1) represents the temperatures and pressures under which the monovariant equilibrium $(F_1) = F_2 + \ldots F_{n+2}$ can occur; now we assume that this curve (F_1) represents nothing else but the phase F_1. [In fig. 2 (II) curve (1) represents therefore, the phase 1, curve 2 the phase 2, etc.]. Now the diagram is no more a P,T-diagram; it is also not a concentration-diagram, for, although we represent in it the $n + 2$ phases, their compositions do not show themselves. It is a schematical reactiondiagram only.

Now it follows from the previous: each phase divides the other into two groups; each of those groups represents a complex of phases and in such a way that both the complexes may be converted mutually.

In the reactionequation the phases of the one complex are situated at the one side, those of the other complex at the other side of the reaction-sign.

Let us apply these considerations to fig. 2 (II), which we consider now as a schematical reaction-diagram. From the position of the phases with respect to one another, the reactions follow:

$$\left.\begin{array}{ccc} 2+3 \rightleftarrows 4+5 & 1+5 \rightleftarrows 3+4 & 1+2 \rightleftarrows 4+5 \\ 1+5 \rightleftarrows 2+3 & 1+2 \rightleftarrows 3+4 & \end{array}\right\} \quad . \quad (53)$$

Consequently we find the same reactions as from the concentration-diagram [fig. 1 (II)]; the difference is only that they may be deduced schematically from fig. 2, quantitatively from fig. 1.

When we consider also the other P,T-diagrams of binary, ternary and quaternary systems, then we find perfect concordance between those and the corresponding concentration-diagrams.

It is apparent from the previous that we may deduce the schematical reactions from both the diagram-types and that the concentration-diagrams have the advantage that they indicate the reactions also quantitatively; the schematical reaction-diagrams have, however the advantage, that they can be drawn in a plane for each system of n components; the concentration-diagrams, however, are situated in a space with n—1 dimensions and consequently they are difficult to draw for systems with more than four components.

We can also obtain schematical reaction-diagrams in other ways.

When we wish to know the reactions quantitatively, then the concentration-diagram has to be known. A similar diagram of a system of n components is represented however in a space with n—1 dimensions and it is difficult to draw it for systems with 5 and more components; but this is unnecessary for our purpose. It is viz. unnecessary for the deduction of the P,T-diagrams to know the reactions quantitatively, but it is sufficient when we know them schematically.

Consequently we put the following question: is it possible to draw for each system with n components without using a space with more than three dimensions, a diagram, which represents all reactions schematically?

We shall discuss one of the different ways, in which this is possible. We imagine an invariant point with the phases A, B, C, D, E, and F; suppose in the monovariant equilibrium (A) the reaction:

$$B+C+D \rightleftarrows E+F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

occurs. We represent each of the phases by a point on a closed curve, e. g. a circle, in this we shall place at the outer side of the circle the letters or figure-signs, belonging to these points).

First we draw in fig. 1 on the circle the point A and we imagine through this point the diameter AA_1 which is not drawn;

as the point A_1 does not represent a phase, we shall draw it on the inner side of the circle. In order to express reaction 54, we place the points E and F at the one side, B, C and D at the other side of the line AA_1.

Fig. 1 gives a graphical representation of reaction 54 and in such a way that any error is excluded. When we had not drawn the point A_1 in it, the representation would be indistinct, as we could not know then, to which monovariant equilibrium the reaction related, so that we might make six suppositions. This doubt, however, is entirely taken away by the point A_1; this means that the reaction relates to the monovariant equilibrium (A).

In this way of representing the position of the points E and F at the one side and that of the points B, C and D at the other side of A is quite arbitrary with respect to one another. Consequently it is not allowed to deduce from fig. 1 the reactions which occur

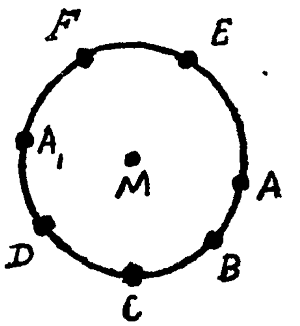

Fig. 1.

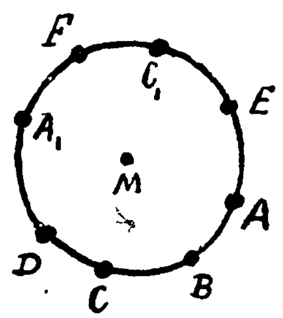

Fig. 2.

in the equilibria (B), (C) etc. Suppose one wishes e. g. to represent the reaction in the equilibrium (C), then for this another figure is wanted, in which we draw a point C_1 within the circle. When this reaction happens to be $A + B + E \rightleftarrows D + F$, we can represent both reactions in fig. 1; then we obtain fig. 2.

As in a system of n components $n + 2$ monovariant equilibria occur, we should want $n + 2$ diagrams for representing those $n + 2$ reactions. We can, however, give to the phases with respect to one another such a position, that all reactions can be represented in a same diagram.

Let us take for an example a quaternary system with the phases A, B, C, D, E, and F. We assume that herein occur the reactions:

$$\left.\begin{array}{ll} A + B + D \rightleftarrows C + E \quad , & A + F \rightleftarrows B + C + D \\ B + C + D \rightleftarrows E + F \quad , & A + B + D \rightleftarrows E + F \\ A + F \rightleftarrows B + C + E \ \text{and} & A + D + F \rightleftarrows C + E \end{array}\right\} \quad . \quad . \quad (55)$$

In order not to make those equations discord, they have been taken from fig. 3 (III).

We imagine that in fig. 3 preliminary the circle is only drawn and on it the points E, E_1, F, and F_1; we take the points E and F arbitrarily. We take the first reaction in order to examine where the point A must be situated; hence it is apparent that A and E must be situated on different sides of the line FF_1. It is apparent from the second reaction that A and F must be situated on the same side of the line EE_1. Consequently the point A must be situated in figure 3 on the arc FE_1; now we draw this in the figure and also the point A_1.

In order to define the position of the point C, we take again the first reaction, hence it follows that C must be situated at the same side of the line FF_1 as the point E; consequently point C is situated

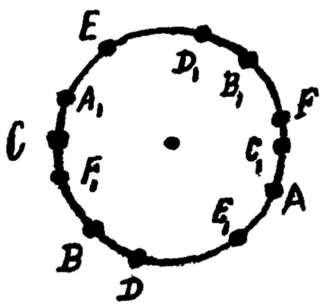

Fig. 3.

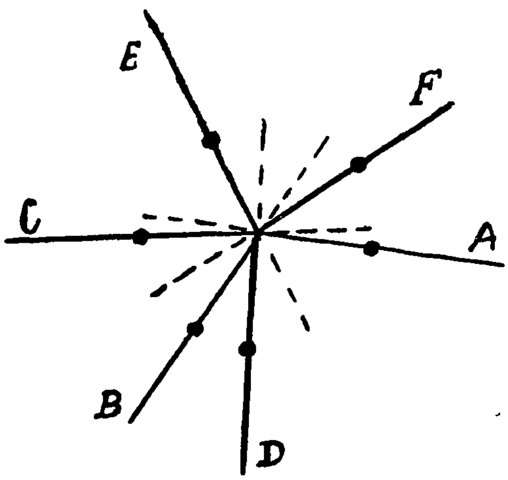

Fig. 4.

on the arc FEF_1. It appears from the second reaction that C and F must be situated on different sides of the line EE_1; consequently point C must be situated on arc EF_1E_1. It follows from both these conditions that point C must be situated on arc EF_1. As on this arc also the point A_1 is situated, we have still to determine the position of C with respect to A_1. This follows at once from the third reaction, from which it appears that we must take C and E on different sides of the line AA_1. Consequently the point C takes its place between A_1 and F_1 and the point C_1, therefore, between A and F.

When we determine also in a similar way the position of the other points, then we obtain fig. 3; this represents, as is easily seen, the six schematical reactions. For the deduction of this figure the six reactions are not exactly wanted, this is not accidental; but it is based on the fact that the reactions are dependent on one another and that of course it is not allowed to take them in discordance.

Now we have represented the six schematical reaction-equations by a schematical reaction-diagram; when these equations were given quantitatively and when we would also express them quantatively, then a representation in space would be necessary; then we should obtain fig. 3 (III). [The six equations 55 are viz. taken from this figure].

Consequently it is apparent from the previous that we may draw a schematical reaction-diagram in a plane for each system of n-components, while a space with n—1 dimensions is wanted for the corresponding concentration-diagram.

Now we shall give another form to fig. 3. For this we draw the diameter A_1A and we prolong it through A; we dot the part A_1M and we omit the letter A_1, which is not necessary now. This line, which we shall also call A, represents the phase A just like the point, situated on this line. When we do the same with the lines B_1B, C_1C etc., then fig. 4 arises. It is evident that we may find from fig. 4, just as from fig. 3, the six reactions schematically.

When we compare this diagram (fig. 4) with the P,T-diagram-type belonging to fig. 3 (III), which is represented in fig. 4 (III), then we see that both figures are perfectly in accordance with one another. The only difference is that in fig. 4 the lines represent a phase and in fig. 4 (III) the lines represent monovariant equilibria.

Hence it is apparent, therefore, that a schematical reaction-diagram and a P,T-diagramtype are represented by the same figure and that the only difference exists in the meaning which we give to the lines.

It might seem strange to the reader that we have deduced in the way followed above a schematical reaction-diagram, which is a perfect representation of a P,T-diagram, without having spoken anywhere in our considerations of temperatures and pressures. When we compare, however, the deduction of fig. 3 and 4 from the reaction-equations 55 with the deduction of fig. 4 (III) from fig. 3 (III) then we see that this deduction is perfectly the same.

From those considerations it is apparent once more that a PT-diagram can be considered as a schematical reaction-diagram of the corresponding concentration-diagram.

The reader himself can deduce that a concentration-diagram can be considered as a schematical representation of the corresponding P,T-diagram.

(*To be continued*).

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