Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

F.A.H. Schreinemakers, In-, mono- and divariant equilibria XII, in: KNAW, Proceedings, 19 I, 1917, Amsterdam, 1917, pp. 816-824

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'

and for the number, the length and the colour of the staminodes, the proportion's of the phaenotypes differ widely in the different sowings, in spite of the fact that the F1 consisted of a single individual; so that the segregation of the hybrids is variable;

2) that in none of the sowings the segregation ratios correspond to those which may be expected from an independent Mendelian segregation.

Chemistry. — "In-, mono- and divariant equilibria". XII. By Prof. F. A. H. Schreinemakers.

(Communicated in the meeting of November 26, 1916).

19. Ternary systems with two indifferent phases.

In communication II we have seen that in ternary systems three types of P, T-diagram [fig. 2 (II), 4 (II) and 6 (II)] exist. When, however, two indifferent phases occur in the invariant point, then, as we shall see further, four types of P, T-diagram exist.

When in the invariant point two indifferent phases occur, then consequently there are three singular phases, they are represented by three points, situated on a straight line. In the types of concentration-diagram of figs. 1, 3, 5 and 7 the indifferent phases are represented by A and B, the singular phases by C, D and E.

In figs. 1 and 3 A and B are situated on the same side, in figs. 5 and 7 on different sides of the line CDE.

In fig. 1 the prolongation of the line AB intersects the prolongation of the line EDC, in fig. 3 the prolongation of AB intersects the line CDE in a point between C and D. [Of course the type of concentration-diagram of fig. 3 remains unchanged, when the point of intersection was situated between D and E].

In fig. 5 the point of intersection of AB and CDE is situated on the line CDE, in fig. 7, however, on the prolongation of the line CDE.

Of course a type of P, T-diagram belongs to each of the four types of concentration-diagram, they are represented in the figs. 2, 4, '6 and '8. We find in each of these diagrams:

the three singular curves:

(M) = C + D + E(A) = B + C + D + E = B + (M) (B) = A + C + D + E = A + (M)

- 2 -

815

and further the curves:

$$(C) = A + B + D + E$$

$$(D) = A + B + C + E$$

$$(E) = A + B + C + D$$

In the singular equilibrium (M) the reaction:

$$C + E \geq D$$

may occur. Hence it follows for the partition of the curves with respect to the (M)-curve:

$$(C)(E) \mid (M) \mid (D)$$
 (1)

In each of the figs. 2, 4, 6, and 8 the curves (C) and (E) must be situated, therefore, at the one side and curve (D) at the other side of the (M)-curve.

In communication I we have deduced the rule for the partition of the curves for the general case, that each curve of a system of n components represents an equilibrium of n + 1 phases. As the (*M*)-curve represents, however, an equilibrium of only n phases, we have to deduce this rule also for this case.

As the (M)-curve coincides with the two other singular curves (A) and (B), we may consider instead of the (M)-curve also curve (A) or (B). In the equilibrium (A) = B + C + D + E, as B takes no part in the reaction as indifferent phase, the reaction:

$$C + E \gtrsim D$$

occurs. Hence follows for the partition of the regions with respect to curve (A):

$$B + C + E \begin{vmatrix} B + E + D \\ B + C + D \end{vmatrix}$$

Each of those regions is limited, besides by curve (A), also by an other curve; the region B + C + E by curve (D), the region B + E + D by curve (C) and the region B + C + D by curve (E). As each region-angle is smaller than 180°, it appears that curve (D) must be situated at the one side, and the curves (C) and (E) at the other side of (A). Consequently we find:

$$(C)(E) \mid (A) \mid (D)$$

۶,

£*

or, as the curves (A) and (M) coincide:

Now already we know, therefore, that in each P, T-diagram-type the curves (C) and (E) must be situated at the one, and curve (D)at the other side of the (M)-curve. It is apparent, however, that this is not sufficient to determine the P, T-diagram-type completely. Now we shall deduce this type for each of the four cases. a) The five phases form a concentration-diagram-type as in fig. 1. From the position of the phases with respect to one another follow the reactions:

and from

	$\begin{array}{c} A+D \rightleftharpoons B+F \\ \dot{A}+C \rightleftharpoons B+E. \end{array}$	 		•	•	•	•	(2) (3)
	$A + C \rightleftharpoons B + D$.	•	•	•	•	•	•	(4)
this:								(D) \
	$(A)(D) \mid (C) \mid (B)(E)$	•	•	•	·	•	٠	(2a)
	$(A)(\underline{C}) \mid (D) \mid (B)(\underline{E})$		•		•		•	(3a)
	$(A)(C) \mid (E) \mid (B)(D)$							(4a)

It appears from 2a, 3a and 4a that the curves (A) and (B) are situated at different sides of each of the three curves (C), (D) and (E). As (A) and (B) are singular curves and they coincide, therefore, with the (\hat{M})-curve, the (M)-curve is consequently bidirectionable. We draw, therefore, in a P, T-diagram the curves (A), (B) and (\hat{M}) as in fig. 2.



At the one side of the (M)-curve we draw curve (D) [fig. 2]; at the other side of the (M)-curve are situated then the curves (C)and (E), of which the position with respect to (A) and (B) has still to be defined. It appears from 3a that (A) and (C) are situated at the one and (B) and (E) at the other side of curve (D); the curves (C) and (E) are situated, therefore, as in fig. 2.

We see that this diagram is also in accordance with 2a and 4a. b) The five phases form a type of concentration-diagram as in fig. 3.

From the position of the phases with respect to one another follows:

$(A)(D) \mid (C) \mid (B)(E).$	•	•	•	•	•	(5)
(A)(C)(E) (D) (B)	•	٠	•	•	•	(6)
$(A) (C) (D) \mid (E) \mid (B) : .$					•	(7)

- 4 -

Because, as it appears from (5), (6), and (7), the singular curves



(A) and (B) are situated on different sides of each of the three curves (C), (D) and (E), it follows again that the (M)-curve is bidirectionable. With the aid of (1) and (6) we find a type of P, T-diagram as in fig. 4. We see that this diagram is also in accordance with (5) and (7).

c) The five phases form a type of concentration diagram as in fig. 5. From the position of the phases with respect to one another follows:

(A) (B) (E) (C) (D) .		•	•	•	(8)
$(A) (B) \mid (D) \mid (C) (E).$	•				(9)
(A)(B) + (E) + (C)(D)					(10)

Hence it appears that the singular curves (A) and (B) are situated on the same side of the three curves (C), (D) and (E); the (M)-curve is, therefore, monodirectionable and the three singular curves (M), (A)and (B) coincide, therefore, in the same direction. We draw, therefore, in a P, T-diagram those three curves as in fig. 6. When we draw



on the one side of the (M)-curve the curve (D), then (C) and (E) must be situated on the other side. Now it follows further from (9) that (C) and (E) must be situated within the angle which is formed by the metastable parts of the curves (D) and (M'. Now it appears from (8) or (10) that those curves (C) and (E) must be situated, as is drawn in fig. 6.

d) The five phases form a type of concentration-diagram as in fig. 7. From the position of the phases with respect to one another follows:

(A)(B)(E) (C) (D)	•	٠	•	•	•	•	(11)
$(A) (B) (E)^{} (D) (C)$		•					(12)
(A)(B)(D) + (E) + (C)		•					(13)

Because, as it appears from (11), (12) and (13) the singular curves (A) and (B) are situated on the same side of each of the three curves (C, (D) and (E), the (M)-curve is, therefore. monodirectionable and the three singular curves (M), (A) and (B) coincide, therefore, in the same direction. Now we draw those three curves in a P, T-diagram, as in fig. 8. When we draw curve (D) at the one side of



the (M)-curve, then (C) and (E) must be situated at the other side. It appears from (12) that (C) must be situated at the one side, and (A), (B) and (E) at the other side of (D); we obtain, therefore a type of P, T-diagram as in fig. 8.

We are also able to find the different types of P, T-diagram by using the three main-types of P, T-diagrams [viz. I, IIA and IIB], which we have deduced in communication X.

In main-type I curve (M), is monodirectionable, so that the three singular curves coincide in the same direction; the P, T-diagram of a system of *n*-components has then the same appearance as that of a system with n-1 components. The P, T-diagram of a ternary

821

system has, therefore, the same appearance as that of a binary system; consequently it exists, as 2 (1), of one two onecurvical bundles. One of the curves of this figure must represent now, the three coinciding singular curves.

When the singular curves are represented by one of the curves of the twocurvical bundle, then fig. 8 arises; when they are represented by one of the two other curves, then fig. 6 arises.

În main-type II curve (M) is bidirectionable; the two other singular curves coincide therefore in opposité direction [fig. 2 X, 3 (X) and 4 (X)].

In main-type II A curve (M) is a middle-curve of the (M)-bundle [fig. 3 (X)]. The type of P, T-diagram consists of:

(\dot{M}) -bundle + 2x other bundles

viz. x bundles on each of the sides of the (M)-bundle. [In fig. 3(X) is x = 2]. The (M)-bundle itself consists of one curve at the one side and three curves at least at the other side of the invariant point; it consists, therefore, of four curves at least. [In fig. 3X of 5].

When we take an (M)-bundle of 4 curves, then, as 5 curves occur in the invariant point, 4 + 2x = 5, consequently $x = \frac{1}{2}$. An (M)bundle of four curves cannot exist, therefore. When we take an (M)-bundle of 5 curves, then 5 + 2x = 5 or x = 0. Consequently the P, T-diagram consists only of an (M)-bundle of 5 curves; we obtain, therefore, a diagram as in fig. 4.

In main-type II B curve (M) is a side-curve of the (\tilde{M}) -bundle [fig. 4 X]. The type of P, T-diagram consists, therefore, of:

(M)-bundle + (2x + 1) other bundles

viz. x bundles at the one side and (x+1) bundles at the other side of the *M*-bundle. [In fig. 4 (X) is x=1]. The *M*-bundle consists of two curves at least at each side of the invariant point; consequently it consists of four curves at least. [In fig. 4 (X) of 6].

When we take an (M)-bundle of four curves, then 4 + 2v + 1 = 5, consequently x = 0. At the one side of the (M)-bundle is situated, therefore, one curve [viz. x + 1 = 1] on the other side not a single curve is situated [viz. x = 0]. Now we obtain the type of P, Tdiagram of fig. 2.

In communication (X) we have deduced the rules:

1

1. The two indifferent phases have the same sign or in other words: the singular equilibrium (M) is transformable into the invariant one and reversally. Curve (M) is monodiffectionable; the three singular curves coincide in the same direction [fig. 1 (X)].

2. The two indifferent phases have opposite sign or in other words: the singular equilibrium (M) is not transformable. Curve (M) is bidirectionable; both the other singular curves coincide in opposite direction [fig. 2 (X), 3 (X) and 4 (X)].

The four types of P, T-diagram [figs. 2, 4, 6 and 8] are in accordance with those rules. In figs. 5 and 7 the singular equilibrium (M) = C + D + E is viz. transformable; in accordance with rule 1 in figs. 6 and 8 the (M)-curve is monodirectionable. In figs. 1 and 3 the singular equilibrium (M) is not transformable; in accordance with rule 2 the (M)-curve is bidirectionable in figs. 2 and 4.

We may also deduce the types of P, T-diagram from the types, which are valid for ternary systems without indifferent phases; we find them in the figs. 2 (II), 4 (II) and 6 (II). [We have to bear in mind that the figs. 4 (II) and 6 (II) must be changed mutually.]

We may consider viz. fig. 1 as a particular case of fig. 1 (II) or 3 (II). When viz. in fig. 1 (II) we let point 5 coincide with a point of the line 2.3, then this concentration-diagram passes into the type of fig. 1; this is also the case when point 4 coincides with a point of the line 12, or point 3 with a point of the line 15 etc. When point 5 coincides with a point of the line 23, then 1 and 4 are the indifferent phases and (1) and (4) the singular equilibria. In the P,-T-diagram of fig. 2 (II) the singular curves (1) and (4) must then coincide; it is apparent from the figure that this coincidence must take place in opposite direction. The P,T-diagram of fig. 2 (II) passes then into the type of fig. 2.

When in fig. 3 (II) point 4 coincides with a point of the line 12, then this concentration-diagram passes also into that of fig. 1. The indifferent phases are then represented by 3 and 5, the singular equilibria by (3) and (5). In the P, T-diagram of fig. 4 (II) the curves (3) and (5) coincide then in opposite direction; then the P, T-diagram becomes the same as that of fig. 1.

In the same way we are also able to deduce the other types of the P, T-diagram. We may viz. consider fig. 3 as a particular case of fig. 3 (II) or 5 (II). Fig. 5 is to be considered as a special case of fig. 3; fig. 7 as a particular case of fig. 5.

۱

When in a ternary system no indifferent phases occur, then, as we have seen in communication II, the curves succeed one another in "diagonal succession". With the aid of this rule we are also able to find the succession of the curves, when two indifferent phases occur. In order to apply this rule to fig: 1 we imagine the point D a little left from the line CE; then we obtain a concentration-diagram of the type of fig. 1 (II), viz. a convex quintangle. The diagonal succession of the phases is then: A-C-E-B-D-A; the succession of the curves in the P,T-diagram must be, therefore, (A)-(C)-(E)-(B)-(D)-(A) or reversally, we see that this is in accordance with fig. 2.

When we imagine the point D a little right from the line CE, then the concentration-diagram forms a monoconcave quintangle, as in fig. 3 (II). The diagonal succession of the phases is then also: A-C-E-B-D, so that the curves have to succeed one another as in fig. 2.

In order to apply the rule to fig. 3 we imagine in this figure the point D a little at the right or at the left of the line CE. In the first case a biconcave quintangle arises [fig. 5 (II)], in the second case a monoconcave quintangle [fig. 3 (II)]. In both cases the diagonal succession of the phases is: $A \rightarrow C - E - B - D - A$; the succession of the curves in the P, T-diagram must be, therefore: (A) - (C) - (E) - (D); this is in accordance with fig. 4.

In order to apply the rule to fig. 5, we imagine also the point D in this figure a little at the right or at the left of CE. In both cases a monoconcave quintangle arises [fig. 3 (II)]. The diagonal succession of the phases is then: A - B - D - C - E or A - B - E - C - D. When we bear in mind that in the P, T-diagram the curves (A) and (B) coincide, then we get a succession of the curves as in fig. 6.

In order to find the succession of the curves in the P, T-diagram which belongs to fig. 7, we imagine in fig. 7 the point D to be situated again a little at the right or at the left of the line CE; then in both cases a biconcave quintangle arises [fig. 5 (II)]. The diagonal succession of the phases is then A-B-D-C-E or A-B-E-C-D. As the curves (A) and (B) coincide, a P, T-diagram as in fig. 8 arises.

In our previous considerations we have shifted a little the point D in each of the figures 1, 3, 5, and 7; it is evident that we might have shifted also the point C or E a little.

20. Quaternary systems with two indifferent phases.

We have seen in communication III that four types of P, T-diagram exist in quaternary systems. When however, 2 indifferent phases occur in the invariant point, then, as we shall see further, 12 types occur. In order to find those types, we might, just as in the case of the ternary systems, construct the different concentrationdiagrams and the type of P, T-diagram belonging to each of those diagrams. Now we shall deduce them, however, without using the concentration-diagrams, with the aid of the three main-types I, IIAand IIB, which we have deduced in communication X.

In main-type I curve (M) is monodirectionable and the 3 singular curves coincide in the same direction. Consequently the P, T-diagram has the same appearance as that of a ternary system. In the types of P, T-diagram of the ternary systems [fig. 2 (II), 4 (II) and 6 (II)] we let one of the curves represent the (M)-curve. Then we find the following diagrams:

$B(M) + B_1 + B_1 + B_1 + B_2$	1			•	•	•	(1)
$B_1(M) + B_2 + B_2 . \qquad .$	•	-		•			(2)
$B_1 + B(M+1) + B_1$.	•					•	(3)-
$B_1 + B(1 + M) + B_2$.	•					•	(4)
$B(M) + B_1 + B_3 . .$	•	•		•	•		(5)
$B_1 + B_1 + B(M+2)$.	•		•	•	•	•	(6)
$B_1 + B_1 + B(1 + M + J)$							(7)

Herein B_1 means an onecurvical bundle, B_2 a twocurvical bundle etc., B(M) indicates a bundle which consists of the (M)-curve only, B(M+1) a bundle, which consists of the (M)-curve and still another curve, etc.

With the aid of main-type Il A we find the diagrams

B(M) +	$B_1 +$	B(1 -	+ M	+	1)	+	B_{ι}		:		(8)
B(M) +	B(1 -	- M -	- 3)	•	•	•		•		•	(9)

 $B(M) + B(2 + M + 2) + \dots + (10)$

With the aid of main-type II B we find yet the diagrams:

The reader himself may easily draw the 12 P, T-diagrams of which the diagrams (1)—(12) are the symbolical representations.

(To be continued).

Leiden, Inorg. Chem. Lab.

ì