Chemistry. — *"In-, mono- and plurivariant equilibria"*. XXVIII. By F. A. H. SCHREINEMAKERS.

Singular equilibria.

In the previous communication we have seen that the "singular part" of an equilibrium determines a phases-reaction, in which not all phases of the equilibrium are participating; and reversally, that a phases-reaction, in which not all phases participate, defines a singular part.

We have called the composants, which participate in the phases-reaction, the singular ones and those who do not participate in the phases-reaction, the indifferent composants.

When we divide the equilibria according to the number of phases-reactions, which may occur in the equilibrium, then we can summarise the results of some of the previous communications in the following way.

I. Equilibria with one phases-reaction.

A. All phases participate in the phases-reaction.

We then have an equilibrium $E(n \cdot r)(r)$; it is monovariant; in a PT-diagram it is represented by a curve; in each point of this curve it is completely defined.

B. There is a singular part.

a. Consequently we have an equilibrium $E(n \cdot r)(r')$; the number of indifferent phases is $R = r - r' > 0$.

When we represent this equilibrium by $E(N \cdot R)$, in which N is the number of indifferent composants, then it has $N - R + 1$ freedoms; when all singular phases have a constant composition, then is $N - R + 1 = n - r + 2$. We may choose T or P as independent variables, but not both together.

It is represented in a PT-diagram by its singular PT-curve; in each part of this curve the singular part is completely defined, but the indifferent part has still $N - R$ freedoms.

b. There is an accidentally singular part.

It is represented in a PT-diagram by the point of contact of its

singular PT-curve with the PT-curve of the equilibrium in its general form. Consequently T and P are completely defined.

II. Equilibria with two or more phases-reactions.

To each phases-reaction belongs, therefore, a singular part. When q phases-reactions occur, so that there are also q singular parts, then we have represented it by $E(n.r)S_q$.

An equilibrium $E(n.r)S_q$ is represented in a PT-diagram by the point of intersection i of its q singular PT-curves.

When there are more than two singular PT-curves, then the directions of those q-curves in point i are corresponding with one another[1]).

Consequently P and T are completely defined · yet the equilibrium may still have freedoms sometimes.

Now we shall apply those general considerations to some of the examples, which have been mentioned in the beginning of the previous communication. In the equilibrium a viz.

$$E(n.3)(2) = solution + (ice + water\ vapour) \quad . \quad . \quad (1)$$

the singular phases are placed again between parentheses, just as previously. The solution contains, besides water, still $n-1$ other substances, which, however, following the supposition, are not volatile.

As only one phases-reaction is possible, in which not all phases participate, it belongs to the group $I.\ B.$; as the singular part is constant, it has $n - 3 + 2 = n - 1$ freedoms.

Consequently its singular PT-curve, by which it is represented in a PT-diagram is the sublimation-curve of the ice; viz. the curve, on which the inversion ice $\rightleftarrows$ water-vapour takes place. In each point of this curve the solution has still $n - 2$ freedoms.

The pressure P_x belonging to a temperature T_x of the equilibrium (1) is found therefore, from the known sublimation-curve of the ice; consequently this pressure P_x is the same for all equilibria (1), no matter how many and which substances the solution contains.

We may express this also in the following way: all equilibria (1) are represented in a PT-diagram by the same curve, how many and which substances the solution contains.

When we cool this system, then P and T change along the sublimation-curve of the ice. When anywhere on this curve a solid

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[1]) Compare: F. A. H. Schreinemakers; these Proceedings 18, 1676.

substance A is separated, then (1) passes into:

$$E(n.4)(2) = A + solution + (ice + watervapour) \quad . \quad . \quad (2)$$

When at further cooling still a second substance is separated, then (2) passes into:

$$E(n.5)(2) = A + B + solution + (ice + watervapour) \quad . \quad (3)$$

etc. The same as above is valid for all those equilibria; consequently they are all represented by the sublimation-curve of the ice; each separation of a new phase diminishes however the number of freedoms with one.

When we cool the system so far that in a point i the number of the phases becomes $n + 2$, then arises an equilibrium:

$$E(n.n+2)S_s = ((A + B\ldots + solution + ice + watervapour)) \quad (4)$$

wherein the double parentheses indicate, that more phases-reactions are possible between the phases, or in other words, that those phases form more singular parts. In this case there are three viz.:

$$(A + B\ldots + solution + ice), \ (A + B\ldots + solution + watervapour)$$

and $$(ice + watervapour)$$

Consequently the equilibrium belongs to group II and it is invariant; it is represented in the PT-diagram by the point of intersection i of: the melting-curve of $A + B \ldots + ice$, the evaporation-curve of $A + B \ldots + solution$ and the sublimation-curve of the ice.

When we cool the equilibrium (1), so that it passes at last into an equilibrium (4), then it proceeds the same PT-curve, therefore; consequently the formation of new phases causes no change of direction of its PT-curve.

When the equilibrium (1) passes into equilibrium (2) in a point r by cooling, then it is possible that the substance A gets accidentally such a composition that it becomes an equilibrium:

$$E(n.4)S_s = ((A + solution + ice + watervapour))$$

with the three singular parts:

$$(A + solution + ice), \ (A + solution + watervapour)$$

and $$(ice + watervapour).$$

The point r then is the point of intersection of the three singular PT-curves. T and P are completely defined then.
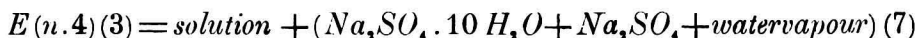
Similar considerations are valid also for equilibria as:

$$E(n.3)(2) = solution + (solid\ benzene + vapour\ benzene) \quad . \quad . \quad (5)$$

$$E(n.3)(2) = solution + (solid\ naphtalene + vapour\ naphtalene) \quad (6)$$

etc.; their singular PT-curves are the sublimation-curves of benzene, naphtalene etc.

An example of the equilibria, mentioned sub (h) we have f.i. in:

$$E\,(n.4)(3) = solution + (Na_2SO_4.10\,H_2O + Na_2SO_4 + watervapour)\ (7)$$

In a PT-diagram it is represented by the dehydratation-curve of the $Na_2SO_4 . 10\,H_2O$, viz. by the PT-curve on which takes place the inversion:

$$Na_2SO_4 . 10\,H_2O \rightleftarrows Na_2SO_4 + watervapour.$$

In each point of this curve the solution still has n—3 freedoms.

The vapour-tension P_x belonging to a temperature T_x is found, therefore, from the known dehydratation-curve of the $Na_2SO_4.10H_2O$; this pressure P_x is the same for all equilibria (7) how many and which substances the solution contains.

When, at decrease of temperature, still other phases are separated, then similar considerations as above are valid.

In the equilibrium:

$$E\,(n.3)(2) = solution + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (8)$$
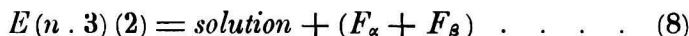
F_α and F_β are two modifications of a solid substance F. It is represented in the PT-diagram by the curve, on which the inversion $F_\alpha \rightleftarrows F_\beta$ takes place; we call this the modification-curve of $F_\alpha + F_\beta$. This equilibrium has n—1 freedoms; consequently the solution has still n—2 freedoms in each point of its PT-curve.

When we take f.i. two modifications of NH_4NO_3 then they can be in equilibrium with their aqueous solution at temperatures and under pressures, which belong to the modification-curve of those two nitrates. As $n = 2$, at each temperature the composition of the solution is defined also.

When we add still a third substance, f.i. alcohol, aceton or NaCl, etc. then the solution has still one freedom in each point of the PT-curve; in a concentration-diagram it is represented then by a curve.

Independent on the number and the character of the substances, which occur in the solution, consequently to each temperature T_x belongs a definite pressure P_x which is defined by the modification-curve of $F_\alpha + F_\beta$.

When we take f.i. α-rhomboic and β-rhomboic NH_4NO_3 then is, in accordance with TAMMANN f.i. for $T_x = 32°$, 40° and 50° the

pressure $P_x = 1,252$ and 550 atmospheres; its termination point towards higher pressures is situated at $T = 64°,2$ and $P = 930$ atmospheres.

Of course similar considerations are valid also for the equilibrium

$$E(n \cdot 3)(2) = vapour + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (9)$$

Above we have said that an equilibrium is represented by its singular PT-curve; this does not involve that, reversally, each point of this curve represents a stable condition of this equilibrium. We have viz. seen already that the equilibrium (1) may be converted by cooling successively into (2), (3) etc. We shall discuss this more in detail with a definite example. For this we take the equilibrium (9) and we shall firstly suppose that it contains two components only (f.i. water and NH_4NO_3; of this salt we take again the two modifications, like above); consequently we have:

$$E(2 \cdot 3)(2) = vapour + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (10)$$

The lowest pressure, under which this equilibrium may exist, is the pressure of the common sublimation-point of $F_\alpha + F_\beta$. This lowest finishing-point of the modification-curve of $F_\alpha + F_\beta$ we call s. The pressure P_s shall differ practically extremely little from zero; the temperature T_s is very little lower than 32°.

We now press together the equilibrium (10), so that it proceeds along the modification-curve from s towards higher pressures; then in each point of this curve the composition of the vapour is completely defined. In a definite point i now as new phase a liquid is formed, so that occurs the equilibrium:

$$E(2 \cdot 4) \, S_s = (solution + vapour + F_\alpha + F_\beta). \quad . \quad . \quad (11)$$

with the three singular parts:

$(solution + vapour + F_\alpha)$, $(solution + vapour + F_\beta)$ and $(F_\alpha + F_\beta)$.

This equilibrium is invariant; the point i is the point of intersection of three singular PT-curves. T_i is somewhat lower than 32°; P_i is smaller than 35 mM. Hg: the vapour-pressure of pure water.

By compressing further (11) is converted at T_i and under P_i into:

$$E(2 \cdot 3)(2) = solution + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (12)$$

which remains at further increase of pressure, till anywhere in a point a of the modification-curve something else takes place.

The equilibria (10) and (12) are represented, therefore, both by the same curve; (10) is however stable only on the part si and (12)

on the part ia. They meet in the point i, where (11) occurs.

The phenomena become otherwise when the system contains more than two components (besides NH_4NO_3 and water f.i. yet alcohol, aceton etc.). Instead of (10) and (12) we then have:

$$E(n.3)(2) = vapour + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (13)$$

$$E(n.3)(2) = solution + (F_\alpha + F_\beta) . \quad . \quad . \quad . \quad (14)$$

which have $n-1$ freedoms; vapour and liquid may have, therefore, still an infinite number of compositions.

We now take an equilibrium (13) of definite composition. When this equilibrium proceeds, starting from s the PT-curve, then in a point i again liquid is formed and consequently arises an equilibrium

$$E(n.4)(2) = solution + vapour + (F_\alpha + F_\beta) \quad . \quad . \quad (15)$$

which is not invariant, but has still $n-2$ freedoms. Equilibrium (15) shall proceed now at further increase of pressure along the singular curve till in a point r the vapour disappears and an equilibrium (14) is formed. This remains at further increase of pressure till anywhere in a point a something else occurs.

Consequently equilibrium (13) exists on part si, (15) on part ir and (14) on part ra of its singular PT-curve.

We have started from an equilibrium (13) which had a definite composition; when we change this, then the points i and r fall also on another place of the curve. As (13) may have infinitely many compositions, there is, therefore, also an infinite number of points i and r.

These points i and r may also coincide to a single point q; this is the case when (15) becomes accidentally an equilibrium

$$E(n.4)S_* = ((solution + vapour + F_\alpha + F_\beta)) \quad . \quad . \quad (16)$$

Then the point q is the point of intersection of the modification-curve with the PT-curves of the two other singular parts:

$$E(n.3)(3) = solution + vapour + F_\alpha \quad . \quad . \quad . \quad (17)$$

$$E(n.3)(3) = solution + vapour + F_\beta \quad . \quad . \quad . \quad (18)$$

When F_α en F_β contain several components, then the PT-curves of (17) and (18) have generally a maximum of temperature; then they intersect the modification-curve in general in 2 points q [1]).

It appears, therefore, from those considerations that the area's of the equilibria (13), (14) and (15) shall partly cover one another on the singular PT-curve. This is also clear in the following way.

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[1]) For ternary systems compare: F. A. H. SCHREINEMAKERS, these Proceedings 16, 1148 etc. (1914).

When we take away the solution from (15), then one of the equilibria (13) arises; when we take away the vapour, then one of the equilibria (14) arises. In connection with our considerations in the previous communication, that, which is said above, follows at once herefrom.

We may assume also that an equilibrium (15) proceeding along its singular PT-curve passes into an equilibrium:

$$E\,(n\,.\,4)\ S_* = (solution + vapour) + (F_\alpha + F_\beta) \quad . \quad (19)$$

Of course this is possible only then, when the solid modifications are sufficiently volatile. As now two phases-reactions may occur, (19) belongs to group II. Consequently the equilibrium is represented by the point of intersection q of the modification-curve with the PT-curve of the equilibrium:

$$E\,(n\,.\,2)\ (2) = solution + vapour \quad . \quad . \quad . \quad . \quad (20)$$

Consequently T_q and P_q are completely defined.

We take again the equilibrium (14). When it proceeds along its PT-curve towards higher pressures, then in a point q of this curve the equilibrium:

$$E\,(n\,.\,4)\ S_* = solution + ((F_\alpha + F_\beta + F_\gamma)) \quad . \quad . \quad . \quad (21)$$

may be formed. Herein the three singular phases represent modifications of the same substance F. We now have the three phases-reactions $F_\alpha \rightleftarrows F_\beta$, $F_\alpha \rightleftarrows F_\gamma$, $F_\beta \rightleftarrows F_\gamma$; the point q is, therefore, the point of intersection of the three modification-curves.
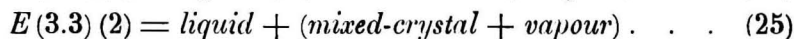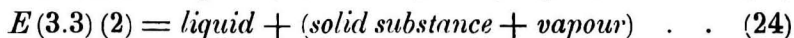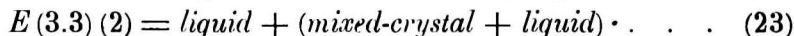
Although T_q and P_q are completely defined, therefore, the solution has yet still $n—2$ freedoms. When it is a binary solution, then it is completely defined; when it contains more than two components, then it may have an infinite number of compositions.

Further it is apparent that T_q en P_q are defined only by the substance F and that they are dependent on the number and the art of the other substances, which occur in the solution.

A similar equilibrium might be realisable when one of the components is f. i. $NH_4 NO_3$. In accordance with TAMMANN at a temperature of 64°,2 and under a pressure of 930 atmospheres the three modifications: α-rhomboic, β-rhomboic and rhomboëdric of $NH_4 NO_3$ exist next to one another. Consequently the equilibrium (21) will be able to exist at $T_q = 64°,2$ and $P_q = 930$ atmospheres, how many and which other substances the solution contains.

Similar considerations are valid when in (21) besides the solution still other indifferent phases are occurring.

We now take the ternary equilibria:

$$E(3.3)(2) = liquid + (solid\ substance + liquid) \quad . \quad . \quad (22)$$
$$E(3.3)(2) = liquid + (mixed\text{-}crystal + liquid) \cdot \quad . \quad . \quad (23)$$
$$E(3.3)(2) = liquid + (solid\ substance + vapour) \quad . \quad . \quad (24)$$
$$E(3.3)(2) = liquid + (mixed\text{-}crystal + vapour) \quad . \quad . \quad (25)$$

We here mean with „solid" substance a solid substance with constant composition. We now distinguish three cases.

a. The singular part contains also the three components.

This is always the case in the equilibria (22) and (23), wherein one of the singular phases is a liquid; in the equilibria (24) and (25) this can be the case only, when the three substances are volatile.

These equilibria belong to group IB; consequently they have $N-R+1$ freedoms. As there is no indifferent component, $N=0$; as there is one indifferent phase, $R=1$. Consequently the equilibria are invariant; temperature, pressure and composition of the phases are, therefore, completely defined.

In a PT-diagram they are represented by a definite point q of their singular PT-curve. In (22) this is the melting-curve, in (24) the sublimation-curve of the solid substance; in (23) it is the curve on which the conversion: mixed-crystal $\rightleftarrows$ liquid takes place; in (25) it is the curve on which the conversion: mixed-crystal $\rightleftarrows$ vapour takes place.

The point q is defined on the singular PT-curve by the fact that those equilibria belong to group $I\,B\,b$; consequently the point q is the point of contact of their singular PT-curve with the PT-curve of the annexed equilibrium in its general form. This is for the equilibrium (22):

$$E(3.3)(3) = liquid + solid + liquid \quad . \quad . \quad . \quad (26)$$

consequently the ternary equilibrium of three phases, which have such composition, that one of them may proceed from the two other ones.

b. the singular part contains two components only.

Of course this may occur only in the equilibria (24) and (25); for this it is necessary that the component, which occurs only in the liquid, is not volatile. As $N=1$ and $R=1$, those equilibria now have one freedom. Consequently they are represented in a PT-diagram by its singular PT-curve; in each point of this curve the composition of the phases is completely defined, therefore.

c. the singular part contains one component only.

This may occur only in the equilibrium (24). As $N=2$ and $R=1$,

this equilibrium has 2 freedoms. We now may, however, represent the number of freedoms also by $n-r+2$, as the two singular phases are constant; it then has $3-3+2=2$ freedoms which is in accordance with $N-R+1$.

Consequently the equilibrium is represented in a PT-diagram by the sublimation-curve of its solid substance, in each point of this curve the liquid has still one freedom.

We assume that in the equilibrium:

$$E(n.3) = liquid + solid \; substance + vapour \quad . \quad . \quad (27)$$

all phases contain the n components. The equilibrium

$$E(n \cdot 3)(3) = liquid + solid \; substance + vapour \quad . \quad . \quad (28)$$

in which the three phases have such composition, that one of them can be composed from the two other ones, is, therefore, monovariant. Consequently it is represented in the PT-diagram by a curve.

Equilibrium (27) also may pass into one of the equilibria:

$$E(n \cdot 3)(2) = (liquid + solid \; substance) + vapour \quad . \quad . \quad (29)$$

$$E(n \cdot 3)(2) = liquid + (solid \; substance + vapour) \quad . \quad . \quad (30)$$

$$E(n \cdot 3)(2) = solid \; substance + (liquid + vapour) \quad . \quad . \quad (31)$$

Each of those equilibria has $N-R+1$ freedoms. Each is represented, therefore, by a definite point of its singular PT-curve. Consequently equilibrium (29) is situated in a point q of the melting-curve of the solid substance, equilibrium (30) in a point r of the sublimation-curve of the solid substance and equilibrium (31) in a point s of the PT-curve, on which the conversion: liquid $\rightleftarrows$ vapour takes place.

Each of those three equilibria belongs to group IBb; to each belongs viz. a definite equilibrium in its general form. In this definite case this equilibrium in its general form is the same for the three equilibria, viz. equilibrium (28).

The points q r and s are situated, therefore, on the PT-curve of equilibrium (28) and they are the points of contact of this curve with the singular PT-curves of the equilibria (29), (30) and (31).

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To be continued.