

Chemistry. — “*In-, mono- and plurivariant equilibria.*” XXVII.
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Singular equilibria.

When in an equilibrium of n components in r phases:

$$E(n.r)(r') = A + B + \dots + L + M \dots + R \dots \quad (1)$$

between the r' phases $L M \dots R$ a phases-reaction

$$\lambda_1 L + \lambda_2 M \dots + \lambda_{r'} R = 0 \dots \dots \quad (2)$$

may occur, then we shall call this equilibrium “singular” and we shall, as in (1), represent it by $E(n.r)(r')$. We call the r' phases, which participate in the phases-reaction, the “singular” phases; the $r-r'$ other ones, which do not participate in this reaction, the “indifferent” phases. Reaction (2) is called: the singular reaction.

When $r' = r$, then it passes into the equilibrium $E(n.r)$, formerly discussed, which is monovariant.

In equilibrium (1) only one singular part occurs, viz. $L M \dots R$, however, there are also equilibria with two and more singular parts. Before discussing more in detail those equilibria, we firstly shall indicate some examples.

I. *Equilibria with one singular part. $E(n.r)(r')$.*

In the equilibrium

a. $E(n.3)(2) = \text{solution} + (\text{ice} + \text{water-vapour}),$

just as we shall do in the following examples, the singular phases are placed between parentheses. It is viz. evident that in this equilibrium, independent on the number of components and on the composition of the solution, the reaction $\text{ice} \rightleftharpoons \text{water-vapour}$ may occur always.

The same is true for equilibria as:

b. $E(n.3)(2) = \text{solution} + (\text{solid benzol} + \text{vapour benzol})$

c. $E(n.3)(2) = \text{solution} + (\text{solid naphthalene} + \text{vapour naphthalene})$

etc. also for the equilibrium:

d. $E(n.4)(2) = A + \text{solution} + (\text{ice} + \text{water-vapour})$

wherein A may represent a solution, a mixed-crystal or a constant solid substance.

When we represent the two modifications of a solid substance F by F_α and F_β , then:

$$e. E(n. 3)(2) = \text{solution} + (F_\alpha + F_\beta)$$

$$f. E(n. 3)(2) = \text{vapour} + (F_\alpha + F_\beta)$$

$$g. E(n. 4)(2) = \text{solution} + \text{vapour} + (F_\alpha + F_\beta)$$

are equilibria, in which $F_\alpha + F_\beta$ is the singular part, independent on the fact how many components the liquid or the vapour contains.

When we represent by Z and $Z \cdot a H_2O$ an anhydric substance and its hydrate, then the equilibria:

$$h. E(n. 4)(3) = \text{solution} + (\text{water-vapour} + Z + Z \cdot a H_2O)$$

$$i. E(n. 5)(3) = A + \text{solution} + (\text{water-vapour} + Z + Z \cdot a H_2O)$$

are also singular ones. Herein A may represent a liquid, a mixed-crystal or a constant solid substance.

In the examples, mentioned above, the singular part consists of constant phases only, viz. of phases, the composition of which is unvariable. There are, however, also equilibria, the singular part of which contains one or more variable phases.

This is f.i. the case in the equilibrium

$$j. E(n. 3)(2) = A + (\text{solid substance} + \text{liquid}),$$

when the liquid gets the same composition as the solid substance, independent on the fact whether this substance is mixed-crystal or it has a constant composition. A may represent a liquid, a vapour, a mixed-crystal or a constant solid substance.

The same is also true for equilibria:

$$k. E(n. 3)(2) = A + (\text{solid substance} + \text{vapour})$$

$$l. E(n. 3)(2) = A + (\text{mixed-crystal} + \text{liquid})$$

$$m. E(n. 3)(2) = A + (\text{mixed-crystal} + \text{vapour})$$

$$n. E(n. 3)(2) = A + (\text{liquid} + \text{vapour}),$$

when the two latter phases have the same composition, and also for the equilibria:

$$o. E(n. 4)(3) = \text{vapour} + (\text{liquid} + A_1 + A_2)$$

$$p. E(n. 4)(3) = \text{liquid} + (\text{vapour} + A_1 + A_2),$$

when the latter three phases have such composition that one of them can be formed from the two other ones.

II. *Equilibria with two or more singular parts.*

We shall represent equilibria with two singular parts by $E(n. r)(r')(r'')$ or by $E(n. r)S_2$. Those equilibria exist only then, when the phases of the two singular parts are different.

We might have examples of such equilibria f.i. in

g. $E(n. 4)(2)(2) = (F_1 + F_2) + (\text{solution} + \text{vapour})$

r. $E(n. 5)(2)(2) = (F_1 + F_2) + \text{solution} + (\text{ice} + \text{water-vapour})$

s. $E(n. 6)(2)(3) = (F_1 + F_2) + \text{solution} + (\text{water-vapour} + Z + Z.aH, O).$

Equilibria, of which two singular parts have one or more phases in common, have always three or more singular parts; in other words: when in an equilibrium two phases-reactions occur, which have one or more phases in common, then always more phases-reactions are possible. In previous communications¹⁾ we have seen that we can deduce all reaction-equations when two of them are known.

Consequently when in the equilibrium $A_1 + A_2 + \text{solution} + \text{vapour}$ a phases-reaction between A_1, A_2 and solution — and a phases-reaction between A_1, A_2 and vapour is possible, then it exists also between A_1 , solution and vapour and between A_2 , solution and vapour. Consequently we have an equilibrium:

t. $E(n. 4) S_4 = ((A_1 + A_2 + \text{solution} + \text{vapour}))$

wherein 4 singular reactions are possible and which contains, therefore, 4 different singular parts. In similar cases we shall place the singular phases in parenthesis.

The equilibria $E(n. n + 2)$ viz. equilibria of n components in $n + 2$ phases belong also to this kind. As in general in those equilibria $n + 2$ singular reactions may occur, they are equilibria $E(n. n + 2) S_q$ in which $q = n + 2$. In special cases, as we have seen previously²⁾ q can be also smaller than $n + 2$; further we still shall refer to an example.

In this specimen of equilibria there may occur also phases, which take part in no single phases-reaction and which are consequently indifferent to all reactions. When we represent by F_α, F_β and F_γ three modifications of a solid substance F , then is

u. $E(n. 4) S_3 = \text{liquid} + ((F_\alpha + F_\beta + F_\gamma))$

a similar equilibrium. Herein are possible the three singular reactions $F_\alpha \rightleftharpoons F_\beta$, $F_\alpha \rightleftharpoons F_\gamma$ and $F_\beta \rightleftharpoons F_\gamma$, but the liquid is indifferent for each of those three reactions. Later we shall discuss a such-like example.

¹⁾ F. A. H. SCHREINEMAKERS; these Proceedings XXIV 882 (1915); 1100 (1916).

²⁾ In previous communications [Proceedings XXV 535, 627, (1916), 754, 860, 939, 1102 (1917)] already several invariant equilibria with indifferent and singular phases have been discussed. In some cases we have even supposed a very special singularity.

Equilibria with one singular part.

We now shall consider more in detail the equilibria, in which only one singular part occurs. When we take the singular part $LM\dots R$ of the equilibrium (1) for itself alone, then we have an equilibrium in r' phases, between which a phases-reaction is possible. Formerly we have seen that such an equilibrium is monovariant and is represented in the PT -diagram by a curve. We call this curve "the PT -curve of the singular part" or also "the singular PT -curve".

We now shall deduce the following property:

an equilibrium $E(n.r)(r')$ is represented in the PT -diagram either by its singular PT -curve or by a point of this curve.

In order to deduce this we imagine that an arbitrary equilibrium E passes through all states, which permit the kind of this equilibrium; to each of those states belongs a definite T and P . Those form in a PT -diagram the PT -area of the equilibrium E . This area may be a field with one or more leaves, a curve, or also a point.

We now take away from E in each state in which it may be found at every time one or more definite phases, but of course repeatedly the same ones; at every time there remains an equilibrium or phases-complex E' . Consequently with each state of E a state of E' is corresponding; everywhere where the region of E is found, we, therefore find also the region of E' . But, as there may be perhaps also states of E' which do not belong to a state of E , the area of E' may perhaps extend itself further. Consequently we may say:

when we take away from an equilibrium one or more phases, then the new PT -area is extended over the first one or it coincides with it.

Now we apply this to the equilibrium $E(n.r)(r')$; when we take away from this the $r-r'$ indifferent phases, then an equilibrium $E(n.r')(r')$ arises, viz. the singular part. This is monovariant, as between all phases a phases-reaction is possible; it is represented in the PT -diagram by a PT -curve.

It now follows from the previous that this PT -curve must extend itself over the area of the equilibrium $E(n.r)(r')$ or that it must coincide with this. The equilibrium $E(n.r)(r')$ is, therefore, either a point of this PT -curve or it coincides with it.

When the equilibrium $E(n.r)(r')$ is represented by its singular PT -curve, then consequently P and T are dependent on one another.

We then may choose or T or P as independent variable ones, but not both at the same time. Yet, as we shall see further, it may have still different other freedoms.

When $E(n, r)(r')$ is represented by a point of its singular PT -curve, then consequently P and T are completely determined.

We may precise more in detail these results in the following way. We take at T_0 and under P_0 an equilibrium:

$$E_0(n, r)(r') = A_0 + B_0 \dots + L_0 + M_0 \dots + Q_0 + R_0 \dots \quad (3)$$

in which $A_0, B_0 \dots$ represent the $r-r'$ indifferent phases and $L_0 \dots, R_0$ the r' singular phases. We represent the phases-reaction in the singular part by:

$$\lambda_1 L_0 + \lambda_2 M_0 \dots + \lambda_{r'} R_0 = 0 \dots \dots \dots (4)$$

We now take at $T_0 + \Delta T$ and $P_0 + \Delta P$ an equilibrium:

$$E(n, r)(r') = A + B \dots + L + M \dots + Q + R \dots \dots (5)$$

the phases of which differ infinitely little from those of the equilibrium E_0 . In a similar way as in (4) we may represent the phases-reaction.

In order to represent the compositions of the phases of the equilibrium E we take n composants. For this we choose the $r-r'$ phases $A, B_0 \dots$; of the r' phases $L, M_0 \dots, R_0$ we may choose $r'-1$ phases only, as those are dependent on one another in accordance with (4). Consequently we take still $n-r+1$ free composants $X, Y \dots$. We represent the composition of an arbitrary indifferent phase I by:

$$I = x X \dots + a A_0 \dots + m M_0 \dots + q Q_0 + \varrho R_0 \dots \dots (6)$$

In order to represent the $r-r'$ indifferent phases $A, B \dots$ of E , we give in (6) to the variables successively the indices $1, 2 \dots (r-r')$.

We shall represent an arbitrary singular phase S by:

$$S = x' X \dots + a' A_0 \dots + m' M_0 \dots + q' Q_0 + \varrho' R_0 \dots \dots (7)$$

In order to represent the r' singular phases $L, M \dots$ of the equilibrium E , we give in (7) to the variables the indices $1, 2 \dots r'$.

It is not necessary now that each of the parts of the singular equilibrium contains the n composants. We see f. i. in the examples $a-g$ that the singular part contains one composant only, in examples h and i that it contains two composants. When we imagine in example j that A represents also a solid substance, then the singular part contains all composants and the indifferent part contains only one.

We now shall assume that these are n_j composants which occur in both parts of the equilibrium; further that there are n_i composants

which occur in the indifferent part only. We call them "indifferent composants" (not: the composants of the indifferent part, for this number is $n_g + n_i$). Further there may be n_s composants, which occur in the singular part only. Consequently we have $n_g + n_i + n_s = n$.

A similar equilibrium may sometimes exist only under very definite conditions, which we shall discuss later. We shall assume here that it exists. Here must be noticed that it may exist always when there is at least one variable phase, which contains all composants and we may assume that this is the case with a liquid. In that case n_i or n_s are zero then. We now shall divide the equations for the equilibrium E into three groups.

The first group relates to the indifferent part, taken for itself only. This is an equilibrium of $n_i + n_g$ composants in $r - r'$ phases; it has, therefore, $n_i + n_g - (r - r') + 2$ freedoms. When we call i the number of variables, which occur in the indifferent part, then, consequently, we may say also that between TP and those i variables there exist $i - (n_i + n_g) + (r - r')$ equations.

The second group relates to the singular part, taken for itself only. This equilibrium is monovariant. When we call s the number of variables which occur in this singular part, then, consequently, there are $s + 1$ equations between PT and those s variables. When we take, therefore, T as independent variable, then P and the s other variables are, consequently completely defined. Consequently this equilibrium is represented by a curve in a PT -diagram.

The third group of equations expresses that the indifferent and the singular part are in equilibrium with one another.

We now assume that as well in the indifferent part as in the singular part there is a variable phase; the first one then contains $n_i + n_g$ composants, the other one $n_s + n_g$ composants. It is sufficient now for the equilibrium that both those phases are in equilibrium with one another. We then still get n_g equations.

Then we have $[i - (n_i + n_g) + r - r'] + (s + 1)n_g$ equations between the $i + s + 2$ variables; consequently the equilibrium has $n_i - (r - r') + 1$ freedoms.

In the following we shall represent n_i viz. the number of indifferent composants by N . When we put $r - r' = R$ then R represents, therefore, the number of indifferent phases. We now shall call an equilibrium $E(n, r)(r')$, in which occur N indifferent composants and $R = r - r'$ indifferent phases, an equilibrium $E(N, R)$. Then we find:

the singular equilibrium $E(N, R)$ has $N - R + 1$ freedoms.

This result is not in accordance with the phase-rule of GIBBS. The number of freedoms is viz. generally smaller than $n-r+2$ and we are limited in the choice of those freedoms in so far, that we may choose T or P as independent variable, but not both together.

This deviation of the phase-rule is however only apparent, in so far that this limitation finds its cause in the conditions which we have attributed to the equilibrium. In a following communication we shall refer to this.

This result is in accordance also with that deduced in a previous communication viz. that an equilibrium $E(n, r)$ has one freedom only. In a similar equilibrium is viz. $N=0$ and $R=0$ so that $N-R+1$ becomes $=1$.

We may assume also that all phases of the singular part have a constant composition, this is a. o. the case in the examples $a-h$.

The second group of equations is reduced then to the one equation:

$$\lambda_1 \zeta_L + \lambda_2 \zeta^M \dots + \lambda_{r'} \zeta_Q = 0 \dots \dots \dots (8)$$

In order to find the third group we must express that one of the variable indifferent phases is in equilibrium with each of the r' singular phases. As, however, in accordance with (4) those are dependent on one another, it is sufficient to take $r'-1$ of these phases; consequently we get $r'-1$ equations.

As in this case $n_s = 0$, follows $n_i + n_g = n$; further is $s = 0$. The total number of equations becomes therefore $i-n+r$, while there are $i+2$ variables consequently the equilibrium has $n-r+2$ freedoms.

This result is in accordance with the number of freedoms following the phase-rule of GIBBS; the only limitation still is that we may not choose P and T at the same time as independent variables. It is also in accordance with the $N-R+1$ freedoms, which must have an equilibrium $E(N, R)$; the number N of the indifferent composants is viz. $n-(r'-1)$; the number R of the indifferent phases is $r-r'$; consequently $N-R+1 = n-r+2$.

It could still also be assumed that the $r-r'$ indifferent phases have all a constant composition. Then the equilibrium can exist, however, only when some conditions are satisfied; we shall refer to this later. When it is not a phases-complex but an equilibrium, then it is invariant.

We may resume the previous in this way.

An equilibrium $E(N, R)$, consequently an equilibrium with one singular part, with N indifferent composants and R indifferent phases, has $N-R+1$ freedoms.

When $N - R + 1 > 0$ then it is represented in a PT -diagram by its singular PT -curve. In each point of this curve the singular part is completely defined, but the indifferent part has still $N - R$ freedoms.

When $N - R + 1 = 0$ then it is represented by a point of this curve.

Consequently it is apparent from the previous that some of the equilibria with one singular part are represented by their singular PT -curve, other ones by a point of this curve. Now it is the question which point of the curve it is.

This case may not occur at an equilibrium of which the singular part is constant; as this has $n - r + 2$ freedoms, r should be $= n + 2$. Then, however, more than one phases-reaction is possible. Consequently we may expect this case only with equilibria, of which the singular part contains also variable phases.

In order to examine this we take the equilibrium $E_0(n.r)(r')$ which we have represented in (3) and in which phases-reaction (4) occurs. We now assume that at other temperatures and pressures there exists an equilibrium, as we have represented in (5); we suppose, however, that this is not an equilibrium $E(n.r)(r')$ but an equilibrium $E(n.r)(r)$. In other words we assume that between the r phases a phases-reaction may occur, which we shall represent by



This equilibrium is monovariant; in a P, T -diagram it is represented by a curve, the direction of which is defined in every point by

$$\frac{dP}{dT} = \frac{\sum(\mu H + \sum(\lambda \eta))}{\sum(\mu V) + \sum(\lambda v)} \quad \dots \quad (10)$$

When this equilibrium proceeds along its PT -curve, then the reaction-coefficients in (9) change continuously. We now assume that in a definite point i all coefficients become zero; we then get the singular equilibrium (3) in which reaction (4) may occur. When we take on this curve points in the vicinity of i , then μ_1, μ_2 , etc. get infinitely small values.

The equilibrium (5) [viz. $E(n.r)(r)$ as we have assumed] is converted therefore, in point i into the equilibrium (3). This can take place, however, only then, when the singular part contains also variable phases. When viz. all phases were constant, then reaction (4) should be valid also always in (9) and there should be possible more than one phases-reaction.

Now the singular part of (3) is represented in the PT -diagram by a curve, the direction of which is defined in each point by:

$$\frac{dP}{dT} = \frac{\sum (\lambda \eta)}{\sum (\lambda v)} \cdot \dots \cdot \dots \cdot \dots \quad (11)$$

As in the point i however μ_1, μ_2 , etc. become zero, consequently (10) passes in this point into (11). Hence it follows, therefore, that the point i , in which the equilibrium (3) exists, is the point of contact of its singular PT -curve with the equilibrium (5).

Consequently we may consider the equilibrium $E_0(n.r)(r')$ as an accidental state of the equilibrium $E(n.r)(r)$; for this reason we call $E_0(n.r)(r')$ an "accidentally" singular equilibrium and $E(n.r)(r)$ the equilibrium in its general form. Consequently it follows from this:

An accidentally singular equilibrium is represented in the PT -diagram by a point; this point is the point of contact of the singular PT -curve [with the PT -curve of the equilibrium in its general form.

We now may prove also that reversally a definite general equilibrium $E(n.r)(r)$ belongs to each invariant equilibrium $E_0(n.r)(r')$ in which the singular part contains one or more variable phases. Consequently we may conclude also:

When an equilibrium with one single singular part is represented in a PT -diagram by a point of its singular PT -curve, then this point is the point of contact of this curve with the PT -curve of the equilibrium in its general form.

Equilibria with two or more singular parts.

When there are in an equilibrium q singular parts, then there are also q singular PT -curves. As the equilibrium must be situated on each of those q singular curves, it is represented, therefore, by the point of intersection of those q curves.

Consequently the temperature T_i and the pressure P_i are completely defined; yet a similar equilibrium may have sometimes still more freedoms, as we shall see further.

When $q=2$, as in the examples $q-s$, then the two singular parts are independent on one another and, therefore, also the directions of the two singular PT -curves in their point of intersection i .

When $q > 2$, as in the examples t and u and in the equilibria $E(n.n+2)$, then the q singular parts are dependent on one another; we can viz., as we have seen previously, deduce from 2 reaction-

equations the $q-2$ other ones. The directions of the q singular PT -curves in their point of intersection i are, therefore, also dependent on one another.

It shall not be necessary to show fully that equilibria with more than 2 singular parts, which are independent on one another, do not exist.

Then we get for the definition of T and P more than two equations which are independent on one another, or in other words: we have in the PT -diagram more than two arbitrary PT -curves. It is evident that only very occasionally they shall go through one point.

(To be continued).

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