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

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Equilibria of n components in r phases.

We take into consideration an equilibrium E and other equilibria, the phases of which differ unfinitely little from those of E. When we express the compositions of the phases in composants, then we may choose them arbitrarily, so that we may take for this also one or more of the phases of the equilibrium E itself. As, therefore, those composants are really also phases of the equilibrium E, we shall call them "real" composants; the other composants, which consequently still rest arbitrary, we call the "free" ones.

We now assume that at a temperature T_0 and under a pressure P_0 an equilibrium

$$E_0 (n . r) = L + M + N \ldots + R \quad . \quad . \quad . \quad . \quad . \quad (1)$$

exists of n components in r phases. In order to represent the phases of an equilibrium:

$$E (n . r) = F_1 + F_2 \ldots + F_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which differ from E_0 $(n . r)$, we must choose n composants. For this we take the r phases $L M \ldots$ of the equilibrium E_0 $(n . r)$, consequently real composants; further we take the $n—r$ free composants $X Y \ldots$; of course one or more of those may also be components. When we represent an arbitrary phase F of the equilibrium $E (n . r)$ by:

$$F = xX + yY \ldots + lL + mM \ldots + qQ + \varrho R \quad . \quad . \quad . \quad (3)$$

wherein $\varrho = 1—x—y \ldots —l \ldots —q$, then we may represent F_1 by giving to all variables in (3) the index 1; F_2 by giving them the index 2, etc.

We now assume that the phases of $E (n . r)$ differ infinitely little from those of $E_0 (n . r)$, viz. F_1 from L, F_2 from $M \ldots$ and F_r from R. Then it appears from (1) and (3) that all variables in (3) should become infinitely small, excepted $l_1, m_2, n_3 \ldots q_{r-1}$ which approach to zero.

When we call the thermodynamical potentials of $F_1 F_2$ etc. $\zeta_1 \zeta_2$ etc. and when we represent by A the form:

$$\zeta - x\frac{\partial\zeta}{\partial x} - y\frac{\partial\zeta}{\partial y} \ldots - l\frac{\partial\zeta}{\partial l} - m\frac{\partial\zeta}{\partial m} \,.\,. - q\frac{\partial\zeta}{\partial q} \quad . \; . \; . \quad (4)$$

then we find for an arbitrary temperature T and pressure P the $r-1$ equations of equilibrium:

$$A_1 = A_2 = \ldots = A_r \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

We obtain $A_1 A_2$ etc. from A by giving in (4) the indices 1, 2 etc. to all variables (ζ also). Of course those equations are valid as well for finite as for unfinitely small values of the variables. Further we still get the $(r-1)(n-1)$ conditions for equilibrium:

$$\left.\begin{aligned} \frac{\partial\zeta_1}{\partial x_1} = \frac{\partial\zeta_2}{\partial x_2} = \ldots = \frac{\partial\zeta_r}{\partial x_r} \\ \frac{\partial\zeta_1}{\partial y_1} = \frac{\partial\zeta_2}{\partial y_2} = \ldots = \frac{\partial\zeta_r}{\partial y_r} \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

and the other ones, which follow herefrom, by substituting x or y by $z\,u \ldots l\,m \ldots$ and q.

When we include in the calculation T and P, then consequently we have $(n-1)\,r+2$ variables and $n(r-1)$ equations; therefore the equilibrium $E(n\,.\,r)$ has $n-r+2$ freedoms. When we put in (5) and (6) $l_1 = 1$, $m_2 = 1$, $n_3 = 1$ and $q_{r-1} = 1$ and further all other variables equal to zero, then we find the conditions for equilibrium for the equilibrium $E_0(n\,.\,r)$; when we put $l_1 = 1 + \Delta l_1$, $m_2 = 1 + \Delta m_2 \ldots q_{r-1} = 1 + \Delta\, q_{r-1}$ and when we take for the other variables infinitely small values, then we find the equations for equilibrium for the equilibrium $E(n.r)$ at $T_0 + \Delta T$ and $P_0 + \Delta P$. From (5) follow the $r-1$ equations:

$$\Delta A_1 = \Delta A_2 = \ldots = \Delta A_r \quad . \; . \; . \; . \; . \; . \quad (7)$$

Further follow from (6) the $(r-1)(n-1)$ equations:

$$\Delta\frac{\partial\zeta_1}{\partial x_1} = \Delta\frac{\partial\zeta_2}{\partial x_2} = \ldots = \Delta\frac{\partial\zeta_r}{\partial x_r} \quad . \; . \; . \; . \; . \; . \quad (8)$$

etc. Herein the sign Δ means that we must take all increases, if necessary those of higher order also. It now follows from (4) that (7) may be satisfied by:

$$\left.\begin{array}{l} \Delta A_1 = -\eta_1 \Delta T + v_1 \Delta P - \Delta \dfrac{\partial \zeta}{\partial l} - \dfrac{1}{2} K_1 \\ \Delta A_2 = -\eta_2 \Delta T + v_2 \Delta P. - \Delta \dfrac{\partial \zeta}{\partial m} - \dfrac{1}{2} K_2 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \Delta A_{r-1} = -\eta_{r-1} \Delta T + v_{r-1} \Delta P - \Delta \dfrac{\partial \zeta}{\partial q} - \dfrac{1}{2} K_{r-1} \\ \Delta A_r \ = -\eta_r \ \Delta T + v_r \ \Delta P - \dfrac{1}{2} K_r \end{array}\right\} \quad . \quad (9)$$

wherein we may give to $\Delta \frac{\partial \zeta}{\partial l}$, $\Delta \frac{\partial \zeta}{\partial m}$ etc. in accordance with (8) each of the indices from 1 to r. Further is

$$K = \left(x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} + \ldots \right)^{(2)} .$$

We now shall mean by the region of an equilibrium: the collection of all complexes, which arise when we add to one another the phases of that equilibrium in all possible ratio's. In a graphical representation we may imagine such a region to be represented by a collection of points. The region of an equilibrium $E(n\,.\,2)$ is, therefore, a straight line, which unites the two phases, namely the part, which is situated between both phases. The region of the equilibrium $E(n\,.\,3)$ is the triangle, which has as angle-points those three phases, etc.

We now may put the question: the regions of two equilibria $E_0(n\,.\,r)$ and $E(n\,.\,r)$ may they have common points at the same temperature and pressure?

In order to represent the region of the equilibrium:

$$E(n\,.\,r) = F_1 + F_2 + \ldots + F_r \,,$$

we must take in the complex

$$a_1 F_1 + a_2 F_2 + \ldots + a_r F_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$a_1\, a_2$ etc. positive and we must give to their ratio's all possible values. In the complex (10) none of the free composants $X\, Y \ldots W$ may occur, in order that this region has one or more points in common with the region of $E_0(n\,.\,r)$. It now follows from (10) that it must be possible that is satisfied:

$$\left.\begin{array}{l} \Sigma\,(ax) = a_1 x_1 + a_2 x_2 + \ldots + a_r x_r = 0 \\ \Sigma\,(ay) = a_1 y_1 + a_2 y_2 + \ldots + a_r y_r = 0 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \Sigma\,(aw) = a_1 w_1 + a_2 w_2 \ \ldots \ . + a_r w_r = 0 \end{array}\right\} \quad . \quad . \quad . \quad (11)$$

As we take under consideration the equilibria $E_0(n.r)$ and $E(n.r)$ at the same P and T, we must put in (9) $\Delta T = 0$ and $\Delta P = 0$. Hence it follows:

$$\Delta \frac{\partial \zeta}{\partial l} = 0 \qquad \Delta \frac{\partial \zeta}{\partial m} = 0 \ldots \Delta \frac{\partial \zeta}{\partial q} = 0 \quad . \quad . \quad . \quad . \quad (12)$$

The stability requires that the magnitudes K_1 K_2 etc. from (9) are positive. As the terms, wich are equal to zero, in accordance with (12), disappear herefrom, we may write:

$$K = x \, \Delta \frac{\partial \zeta}{\partial x} + y \, \Delta \frac{\partial \zeta}{\partial y} + \ldots w \, \Delta \frac{\partial \zeta}{\partial w}. \quad . \quad . \quad . \quad . \quad (13)$$

When we add K_1 K_2 etc., after having multiplied them successively with a_1 a_2 etc., then follows:

$$\Sigma (a x) \, . \, \Delta \frac{\partial \zeta}{\partial x} + \Sigma (a y) \, . \, \Delta \frac{\partial \zeta}{\partial y} \ldots + \Sigma (a w) \, . \, \Delta \frac{\partial \zeta}{\partial w} \quad . \quad . \quad (14)$$

which form must be positive. Consequently it is impossible to satisfy the equations (11), as (14) should then be equal to zero. Consequently we find:

the regions of the stable equilibria $E_0(n.r)$ and $E(n.r)$ may never have points in common at the same temperature and under the same pressure.

The conjugation-line of the two phases of an equilibrium $E_0(n.2)$, therefore, never intersects the conjugation-line of the equilibrium $E(n.2)$; the three-phases-triangle of an equilibrium $E_0(n.3)$, therefore, never intersects the three-phases-triangle of the equilibrium $E(n.3)$, etc. In the previous communication we have deduced this property for a special case, viz. for an equilibrium $E(3.2)$ in quite another way. We also easily find this property in the following way. Suppose the regions of the equilibria $E_0(n.r)$ and $E(n.r)$ have a point in common; then this point may represent either a complex of the phases of the equilibrium E_0 or one of the phases of the equilibrium E. As T and P are, however, the same for both complexes, the complex with the largest thermodynamical potential shall be converted into that with the smallest one. Consequently both complexes cannot exist at the same time or in other words, the two regions cannot have a point in common.

The deductions above are no more valid when we keep no more constant either the temperature or the pressure, or both. Then we find:

the regions of the equilibrium $E_0(n.r)$ at T_0 and of the equilibrium

$E(n\,.\,r)$ at $T_0 + \Delta T$ have points in common, also when the pressure for both is the same.

We shall represent an equilibrium of n components in r phases, when a phases-reaction is possible between those r phases, by $E(n.\,r)\,(r)$. We now assume that at T_0 and P_0 an equilibrium

$$E_0\,(nr)\,(r) = L + M + N \ldots + Q + R \quad . \quad . \quad . \quad . \quad (15)$$

exists; we represent the phases-reaction by

$$\lambda_1\,L + \lambda_2\,M \ldots + \lambda_{r-1}\,Q + \lambda_r\,R = 0 \quad . \quad . \quad . \quad . \quad (16)$$

As, in accordance with (16) those phases are dependent on one another, we may take only r—1 of them as composants; for this we take $MN \ldots R$. We now represent an arbitrary phase F in stead of by (3) by

$$F = xX + yY \ldots + mM + nN \ldots qQ + \varrho R \quad . \quad . \quad (17)$$

viz. by r—1 real and $n-r+1$ free composants. The phases of an arbitrary equilibrium:

$$E\,(n\,.\,r) = F_1 + F_2 \ldots + F_r \quad . \quad . \quad . \quad . \quad . \quad (18)$$

we represent again by giving in (17) the indices $1, 2, \ldots r$ to the variables. When we represent again by A

$$\zeta - x\frac{\partial\zeta}{\partial x} - y\frac{\partial\zeta}{\partial y} \ldots - m\frac{\partial\zeta}{\partial m} \ldots - q\frac{\partial\zeta}{\partial q} \quad . \quad . \quad . \quad (19)$$

then for the equilibrium $E(n\,.\,r)$ at arbitrary P and T the r—1 equations

$$A_1 = A_2 = \ldots = A_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

are following again and $(r-1)\,(n-1)$ equations like in (6).

We now assume again that the phases of the equilibrium $E(n\,.\,r)$ differ infinitely little from those of $E_0\,(n\,.\,r)\,(r)$. When the composition of F_1 must approach to L, then it appears from (17) that we must give to the quantities $x_1\,y_1$ etc. of the free composants the infinitely small values Δx_1 Δy_1 etc. In connection with the composition of L, which is following from (16) it is apparent that we must put:

$$m_1 = -\frac{\lambda_2}{\lambda_1} + \Delta\,m_1 \qquad n_1 = -\frac{\lambda_3}{\lambda_1} + \Delta\,n_1 \ldots q_1 = -\frac{\lambda_{r-1}}{\lambda_1} + \Delta\,q_1$$

wherein Δm_1 etc. are infinitely small.

When the composition of F_2 approaches to M, then we must put $m_2 = 1 + \Delta m_2$ and further we must replace all other variables $x_2\,y_2$ etc. by the infinitely small values $\Delta x_2\,\Delta y_2$ etc. For the other phases $F_2 \dots F_r$ we find that all variables must be infinitely small, excepted

$$n_3 = 1 + \Delta n_3 \dots q_{r-1} = 1 + \Delta q_{r-1}.$$

In order to satisfy (20) we now have, as follows from (19):

$$\left.\begin{aligned}
\lambda_1 \Delta A_1 &= -\lambda \ \eta_1 \Delta T + \lambda_1 v_1 \Delta P + \lambda_2 \Delta \frac{\partial \zeta}{\partial m} + \lambda_3 \Delta \frac{\partial \zeta}{\partial n} \dots \\
&\qquad \dots + \lambda_{r-1} \Delta \frac{\partial \zeta}{\partial q} - \frac{1}{2} \lambda_1 K_1 \\
\Delta A_2 &= - \eta_2 \Delta T + v_2 \Delta P - \Delta \frac{\partial \zeta}{\partial m} - \frac{1}{2} K_2 \\
&\dots\dots\dots\dots\dots\dots \\
\Delta A_{r-1} &= - \eta_{r-1} \Delta T + v_{r-1} \Delta P - \Delta \frac{\partial \zeta}{\partial q} - \frac{1}{2} K_{r-1} \\
\Delta A_r &= - \eta_r \Delta T + v_r \Delta P - \frac{1}{2} K_r
\end{aligned}\right\} \quad . \ . \quad (21)$$

wherein again

$$K = \left(\Delta x \,.\, \frac{\partial \zeta}{\partial x} + \Delta y \,.\, \frac{\partial \zeta}{\partial y} + \dots \right)^{(2)}.$$

Further we may give, as it shall appear at once, to $\Delta \frac{\partial \zeta}{\partial m}$ etc. all indices from 1 to r. We yet have viz. the $(r-1)(n-1)$ equations (6) from which follows:

$$\Delta \frac{\partial \zeta_1}{\partial x_1} = \Delta \frac{\partial \zeta_2}{\partial x_2} = \dots = \Delta \frac{\partial \zeta_r}{\partial x_r} \quad . \ . \ . \ . \quad (22)$$

and the other ones, which we get herefrom by substituting x by $y \, z \dots m \dots q$.

When we add the equations (21) after having multiplied ΔA_2 with λ_2, ΔA_3 with λ_3 etc., then we get, as $\Delta A_1 = \Delta A_2 = \dots = \Delta A_r$, and as $\Sigma(\lambda)$ must be zero in accordance with (16):

$$- \Sigma(\lambda\eta) \,.\, \Delta T + \Sigma(\lambda v) \,.\, \Delta P = \frac{1}{2} \Sigma(\lambda K) \quad . \ . \ . \quad (23)$$

Further from (21) still the $r-2$ equations follow:

$$\left.\begin{aligned}
(\eta_r - \eta_2) \Delta T + (v_2 - v_r) \Delta P &= \Delta \frac{\partial \zeta}{\partial m} \\
&\dots\dots\dots\dots \\
(\eta_r - \eta_{r-1}) \Delta T + (v_{r-1} - v_r) \Delta P &= \Delta \frac{\partial \zeta}{\partial q}
\end{aligned}\right\} \quad . \ . \quad (24)$$

wherein K_2 etc. have been omitted, as they are infinitely small with respect to the terms, which are already written down.

Consequently we have in (22), (23) and (24) $rn-n$ equations between the $rn-r+2$ variables for definition of the equilibrium $E(n.r)$ at $T_0+\Delta T$ and under $P_0+\Delta P$.

Firstly we now put the question: when an equilibrium $E_0(nr)(r)$ exists at T_0 and under P_0, still other equilibria $E(n.r)$ may they exist at the same temperature and under the same pressure?

As the equilibrium now has still $n-r$ freedoms only, and as r must be 2 at least, this case may, therefore, occur only with systems with 3 or more components. As further we must put $\Delta T=0$ and $\Delta P=0$, it follows from (23):

$$\lambda_1\left(\Delta x_1\ \frac{\partial \zeta_1}{\partial x_1}+\Delta y_1 . \frac{\partial \zeta_1}{\partial y_1}\dots\right)^{(2)}+\lambda_2\left(\Delta x_2 . \frac{\partial \zeta_2}{\partial x_2}+\Delta y_2 \frac{\partial \zeta_2}{\partial y_2}\dots\right)^{(2)}+\dots=0\ .(25)$$

The stability requires that each of the forms in parenthesis is positive. Of course the increases in (25) are not independent on one another, but they are united by the equations (22) and (24), wherein $\Delta T=0$ and $\Delta P=0$. Hence it appears, therefore, that it shall depend on many conditions whether (25) may be satisfied or not. When this is not the case, then at T_0 and under P_0 only the equilibrium $E_0(n\,r)(r)$ exists; when it is really the case then still also other equilibria $E(n.r)$ exist, which then have $n-r$ freedoms. Later we shall illustrate this by treating an example.

Let us assume that (22), (24) and (25) may be satisfied by definite values of the increments Δx_1 Δy_1 etc. Then a definite equilibrium $E(n.r)$ exists. However, the equations may be satisfied also by giving the opposite sign to all increments; consequently also an other equilibrium $E^1(n.r)$ exists. We shall call two equilibria, which satisfy this condition the reflected images of one another, because, in a graphical representation, they are looking somewhat alike. Consequently we may say, also in connection with the previous:

when at T_0 and under P_0 besides the equilibrium $E_0(n\,r)(r)$ still other equilibria $E(n.r)$ exist, then they are two by two the reflected image of one another; the regions of those equilibria have no points in common.

We now may also answer the question: when an equilibrium $E_0(n\,r)$ (r) exists at T_0 and under P_0, which other equilibria $E(n.r)$ are existing then under the same pressure but at the temperature $T_0+\Delta T$?

In order to answer this question we put $\Delta P = 0$; (23) becomes then:

$$\Sigma (\lambda \eta) . \Delta T = -\frac{1}{2} \Sigma \lambda \left(\Delta x . \frac{\partial \zeta}{\partial x} + \Delta y . \frac{\partial \zeta}{\partial y} \ldots \right)^{(2)} \quad . \quad . \quad (26)$$

The equations (22) and (24) are homogeneous and of the first degree with respect to ΔT and the other increments. We may satisfy those equations by taking all increments of the same order, but ΔT of the order $(\Delta x)^2$. In the equations (22) and (24) at first approximation all terms with ΔT may disappear. Then it follows from (24):

$$\Delta \frac{\partial \zeta}{\partial m} = 0 \qquad \Delta \frac{\partial \zeta}{\partial n} = 0 \ldots \Delta \frac{\partial \zeta}{\partial q} = 0 \quad . \quad . \quad . \quad . \quad (27)$$

with the indices 1 to r. We may use those equations in order to simplify (26).

$\Sigma (\lambda \eta)$ in (26) is the increase of entropy when in the equilibrium $E_0 (n . r) (r)$ the phases-reaction (16) occurs. We imagine that the reaction proceeds in that direction, at which the entropy increases; then $\Sigma (\lambda \eta)$ is positive and the signs of λ_1 λ_2 etc. are defined.

We now distinguish three cases.

1. the second part of (26) is always positive.

Then (26) can only be satisfied by giving a positive value to ΔT. Hence follows:

equilibria $E (n . r)$ exist only at temperatures higher than T_0; or also: the temperature T_0 of the equilibrium $E_0 (n r) (r)$ is a minimum-temperature for the equilibria $E (n . r)$.

2. The second part of (26) is always negative.

We find: equilibria $E (n . r)$ exist only at temperatures lower than T_0; or also: the temperature T_0 of $E_0 (n r) (r)$ is a maximumtemperature for the equilibria $E (n . r)$.

3. The second part of (26) may be positive, negative and zero.

We find: equilibria $E (n . r)$ exist as well at T_0 as at higher and lower temperatures; the temperature T_0 of the equilibrium $E_0 (n.r) (r)$ is nor maximum- nor minimum-temperature for the equilibria $E (n.r)$.

Just as above we find that the equilibria existing at $T_0 + \Delta T$ (ΔT positive, negative or zero) are two by two the reflected image of one another and that their regions have no points in common.

As the question: when at T_0 and under P_0 an equilibrium $E_0 (n r) (r)$ exists, which equilibria $E (n . r)$ exist then at the same temperature but under a pressure $P_0 + \Delta P$, leads to the same results, we shall not discuss this question.

We now shall put the question: when at T_0 and under P_0 exists an equilibrium $E_0\,(n\,r)\,(r)$, another equilibrium $E\,(n\,r)\,(r)$ can it exist at $T_0 + \Delta T$ and under $P_0 + \Delta P$ and under which conditions? As in the equilibrium $E_0\,(n\,r)\,(r)$ the phases-reaction (16) occurs, must be:

$$\Sigma\,(\lambda) = \lambda_1 + \lambda_2 + \ldots + \lambda_r = 0 \quad . \; . \; . \; . \; . \quad (27)$$

In accordance with our assumption, also a phases-reaction may occur in the equilibrium $E\,(n\,r)\,(r)$; we represent this by:

$$\lambda'_1\,F_1 + \lambda'_2\,F_2 \ldots + \lambda'_r\,F_r = 0 \quad . \; . \; . \; . \; . \quad (28)$$

In accordance with (17) and (18) it must be possible to satisfy:

$$\Sigma\,(\lambda'\,x) = 0 \qquad \Sigma\,(\lambda'\,y) = 0 \ldots \Sigma\,(\lambda'\,m) = 0 \ldots \Sigma\,(\lambda'\,q) = 0 \quad (29)$$

As the phases of $E\,(n\,r)\,(r)$ and $E_0\,(n\,r)\,(r)$ differ infinitely little in composition, they pass into:

$$\left.\begin{array}{l} \Sigma\,(\lambda' . \Delta\,x) = 0 \qquad \Sigma\,(\lambda' . \Delta\,y) = 0 \ldots \\ \Sigma\,(\lambda'\,m) = -\,\lambda'_1\,\dfrac{\lambda_2}{\lambda_1} + \lambda'_2 + \Sigma\,(\lambda'\,\Delta\,m) = 0 \\ . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \\ \Sigma\,(\lambda'\,q) = -\,\lambda'_1\,\dfrac{\lambda_{r-1}}{\lambda_1} + \lambda'_{r-1} + \Sigma\,(\lambda'\,\Delta\,q) = 0 \end{array}\right\} \quad . \quad (30)$$

From this we find that at first approximation the $n - r + 1$ equations must be satisfied:

$$\left.\begin{array}{l} \Sigma\,(\lambda\,.\,\Delta x) = \lambda_1\,\Delta x_1 + \lambda_2\,\Delta x_2 \ldots + \lambda_r\,\Delta x_r = 0 \\ . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \\ \Sigma\,(\lambda\,.\,\Delta w) = \lambda_1\,\Delta w_1 + \lambda_2\,\Delta w_2 \ldots + \lambda_r\,\Delta w_r = 0 \end{array}\right\} \quad . \; . \quad (31)$$

wherein $\lambda_1\,\lambda_2$ etc. have the values from (16). Those $n - r + 1$ conditions contain only increments, which refer to the quantities of the free composants. We now have for the definition of the equilibrium $E\,(n\,r)\,(r)$ at $T_0 + \Delta T$ and under $P_0 + \Delta P$ the $rn - n$ equations (22), (23) and (24) and further the $n - r + 1$ equations (31), consequently $r\,n - r + 1$ equations between the $n\,r - r + 2$ variables. The equilibrium $E\,(n\,r)\,(r)$ has, therefore, one freedom.

We cannot satisfy those equations by taking ΔT or ΔP or both of higher order than the other increases, but we may satisfy them by taking all increments of the same order.

Then it follows from (23):

$$\frac{\Delta P}{\Delta T} = \frac{\Sigma(\lambda\eta)}{\Sigma(\lambda v)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (32)$$

Consequently to each change of temperature ΔT belongs a change in pressure ΔP, defined by (32). We find, therefore: when an equilibrium $E_0 (n\,r)(r)$ exists at T_0 and under P_0, then at $T_0 + \Delta T$ also an equilibrium $E(n\,r)(r)$ exists, of which the composition of the phases and the pressure are completely defined (viz. ΔP by 32); also at $T_0 - \Delta T$ a similar equilibrium exists; both are the reflected image of one another.

We also may prove that the regions of the equilibria $E_0 (n\,r)(r)$ and $E(n\,r)(r)$ have no points in common. When this should be the case, then, as we have seen previously, we must be able to satisfy

$$\Sigma(a \,.\, \Delta x) = 0 \qquad \Sigma(a \,.\, \Delta y) = 0 \ldots \Sigma(a \,.\, \Delta w) = 0 \;. \quad . \quad (33)$$

wherein $a_1\, a_2$ etc. are positive. However, $\Delta x_1\, \Delta x_2$ etc. satisfy the equation (31) in which the coefficients $\lambda_1 \lambda_2$ etc. have different signs; consequently they never can satisfy (33).

This is, however, only true for equilibria $E(n\,r)(r)$ in which $r \leqq n$. At the deduction is viz. supposed that there is one free composant at least, consequently $n - r + 1 \geqq 1$ or $r \leqq n$. When $r = n + 1$ then the two regions have really points in common.

Consequently we may represent in a PT-diagram by a curve an equilibrium $E(n\,r)(r)$. Further we shall divide those equilibria into "transformables" and "intransformables". We shall viz. call the equilibrium transformable when we can proceed a finite part of the PT-curve with a definite complex of the r phases; we call it intransformable when we cannot convert the equilibrium of a temperature T in one of the temperature $T + \Delta T$, unless we add one or more of the components.

It appears from our previous considerations that for $r = n + 1$ the equilibria are transformable and for $r < n + 1$ intransformable.

A binary equilibrium $E(2 \,.\, 3)(3)$ f.i. solid + liquid + vapour is, therefore, transformable; we can realise a finite part of its PT-curve with a complex of definite composition.

The binary equilibrium $E(2 \,.\, 2)(2)$ or in general the equilibrium $E(n \,.\, 2)(2)$ of n components f.i. liquid + vapour is intransformable; when we will bring it from a temperature T of its PT-curve towards a temperature $T + \Delta T$, then we must add or remove a little of one or more of the components.

In accordance with our considerations an equilibrium $E(n\,.\,2)\,(2)$ $=$ solid $+$ liquid ought to be intransformable, also when the solid substance has an invariable composition. This is, however, not the case; here the PT-curve is viz. the melting-line of the solid substance and it is clear that we can realise it without it is necessary to change the composition of the complex. Yet this contradiction is only apparent. Solid substance and liquid have viz. the same composition and although they are built up out of n different other substances, yet there is one composant only. Consequently it is not an equilibrium $E(n\,.\,2)\,(2)$ but an equilibrium $E(1\,.\,2)\,(2)$ and it must, therefore, be transformable.

In general an equilibrium $E\,(n\,.\,r)\,(r)$ in which r—1 of the phases have a constant composition and only one of the phases is variable, is an equilibrium $E\,(r—1.\,r)\,(r)$ and consequently transformable.

When an equilibrium $E\,(n\,r)\,(r)$ goes along its PT-curve, then the values of $\Sigma\,(\lambda\eta)$ and $\Sigma(\lambda v)$ change from point to point. When $\Sigma(\lambda\eta)$ becomes zero in a point, then, as is apparent from (32), the tangent in this point is parallel to the T-axis; consequently the pressure in this point is maximum or minimum. In order to examine this further, we must take now into the equations (21) also terms with ΔT^2. Instead of (23) we then find an equation of the form: $\Delta P = \alpha\,.\,\Delta T^2$. The pressure in this point is, therefore, maximum when $\alpha < 0$ and minimum when $\alpha > 0$.

When in another point $\Sigma\,(\lambda v)$ becomes $= 0$, then the tangent in this point is parallel to the P-axis. Instead of (23) we now find: $\Delta T = \beta\,.\,\Delta P^2$. Consequently the temperature is maximum when $\beta < 0$ and minimum when $\beta > 0$.

Therefore, we find: the temperature of an equilibrium $E\,(n\,.\,r)\,(r)$ is maximum or minimum, when the volume does not change at the phases-reaction; the pressure is maximum or minimum, when the entropy does not change, consequently when at the phases-reaction no heat is absorbed or given away.

When we apply this to a binary equilibrium: solid substance $+$ liquid $+$ vapour, consequently to an equilibrium $E(2,\,3)\,(3)$, then follows at once the known property, which defines in this system the position of the point of maximum temperature and pressure.

When an equilibrium $E\,(n.\,r)\,(r)$ goes along its PT-curve, then the ratio's of the reaction-coefficients change from point to point; in definite points then one or more of those coefficients may become zero. When in a point a, consequently at the temp. T_a and under the pressure P_a f.i. λ_1 becomes zero, then reaction (16) passes into:

$$\lambda_1 M + \lambda_2 N \ldots + \lambda_{r-1} Q + \lambda_r R = 0,$$

so that the phase L does not take part into the reaction. The tangent in point a to the PT-curve is defined then by (32) in which, however, the terms $\lambda_1 \eta_1$ and $\lambda_1 v_1$ disappear. We now take away from the equilibrium $E(n.r)(r)$ the phase L, while we let unchanged temperature and pressure; then a new equilibrium $E(n.r-1)(r-1)$ arises. This equilibrium is also represented in a PT-diagram by a curve, which goes of course through the point a. The direction of the PT-curve $E(n.r-1)(r-1)$ in point a is, however, defined also by an equation of the form of (32); herein now also the terms $\lambda_1 \eta_1$ and $\lambda_1 v_1$ are wanted, while the other terms have the same values as for the equilibrium $E(n.r)(r)$. Consequently the two curves touch one another in the point a. As the same discussion is valid also when more coefficients become zero, we get, therefore:

when at T_a and under P_a some phases (f.i. r') of the equilibrium $E(n.r)(r)$ do not participate in the phases-reaction, then the PT-curve of $E(n.r)(r)$ and that of $E(n.r-r')(r-r')$ touch one another in the point a.

In general we may imagine, therefore, $r-1$ equilibria $E(n.r-1)(r-1)$, further $\frac{1}{2}r(r-1)$ equilibria $E(n.r-2)(r-2)$ etc., the PT-curves of which come in contact with that of the equilibrium $E(n.r)(r)$.

When we apply this f.i. to the binary equilibrium $E(2.3)(3) =$ solid substance + liquid + vapour, then herefrom at once the known property follows, that the PT-curve of this equilibrium touches that of the equilibrium $E(2.2)(2) =$ liquid + vapour; that of the equilibrium $E(2.2)(2) =$ solid substance + vapour, consequently the sublimation-line of the solid substance, and that of the equilibrium $E(2.2)(2) =$ solid substance + liquid, consequently the melting-line of the solid substance.

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