Chemistry. — *"Equilibria in systems, in which phases, separated by a semipermeable membrane"* XVI. By F. A. H. SCHREINEMAKERS.

Some general considerations.

We imagine in the diagrams of the previous communications to be drawn a straight line through the point W. If this line is situated totally out of the region of dimixtion, then the $O.W.A.$ of the liquids of this line increases, according to those liquids being situated further from the point W. If this line intersects a region of dimixtion of two or three liquids, then the same is true for the parts of this line situated outside this region. If we take f.i. the line Wg (fig. 2 XIII); its point of intersection with curve m_1a_1 is called s. The $O.W.A.$ of the liquids of this line then increases from W to s and from a_2 to g; the $O.W.A.$ of liquid a_2 is larger also than that of liquid s. On the line Wm_1m_2 (fig. 2 XIII) the $O.W.A.$ increases from W to m_1 and further from m_2 towards points, situated further from point W; the $O.W.A.$ of the liquids m_1 and m_2 is the same, however.

As the liquids of a straight line going through point W can arise from one another by taking in — or losing water, we may say therefore:

of two stable substances, which can be converted into one another by taking in — or losing water, the liquid with the smallest content of water has the greatest $O.W.A.$ and the liquid with the greatest content of water has the smallest $O.W.A.$ If, however, the two liquids can be in equilibrium with one another, then they have the same $O.W.A.$ (f.i. m_1 and m_2 in fig. 2 XIII).

This rule is a special case of a more general rule which we shall discuss. We take an equilibrium, in which, at taking in and losing a little water, a phases-reaction occurs, viz. a reaction, at which the quantities, but not the compositions of the phases change. Let us take f.i. the system

$$L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1 XV.}$$
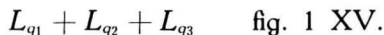
Herein when taking in water occurs the reaction

$$L_{q_3} + water \rightarrow L_{q_1} + L_{q_2}$$
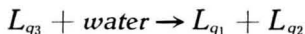
and when losing water the reaction:

$$L_{q_1} + L_{q_2} - water \rightarrow L_{q_3};$$
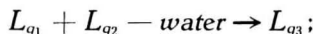
the composition of the phases does not change, therefore, but the quantities change. The same is valid also for the equilibrium of the three liquids q_1 q_2 and q_3 in fig. 2 XV; for the ternary equilibria:

$$X + Y + L_c, \quad H + Y + L_d \quad \text{fig. 2 V;} \qquad Y + D + L_c \quad \text{fig. 2, 3 V}$$
$$X + D + L_d \quad \text{fig. 2, 3 V;} \qquad F + L_{q_1} + L_{q_2} \quad \text{fig. 3 XV}$$
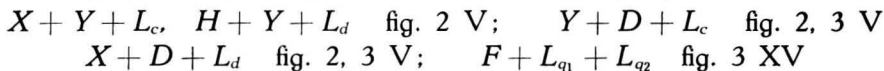
and for the binary equilibria:

$$H + L_a, \quad H + Y, \quad X + L_b \qquad \text{fig. 2 V.}$$
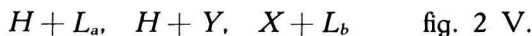
In all those equilibria viz. at taking in- and losing a little water a phases-reaction occurs; consequently the $O. W. A.$ does not change; we shall call similar systems: "osmotic invariant".

In a system of n components, which consists of n or more phases, at taking in- or losing water always a phases-reaction can occur, unless in special cases. If we take f.i. three phases of a ternary system, which can be represented accidentally by three points, situated on a straight line, which does not go through the point W, then between those phases a phases-reaction is possible, but this is not the case when taking in or losing water.
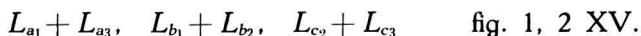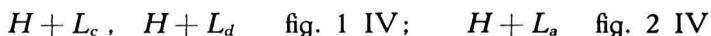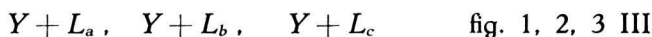
If a system of n components consists of less than n phases, then in this system generally no phases-reaction is possible when taking in or losing water, unless the compositions of the phases satisfy certain conditions. This is f.i. the case in the ternary equilibria:

$$D + L_w, \quad D + L_v \quad \text{fig. 2 IV,} \qquad L_{m_1} + L_{m_2} \quad \text{fig. 2, 3 XIII.}$$

They are, although they consist of two phases only, yet osmotic invariant.

If in a system by taking in and losing water one or more of the phases change their composition, then the $O.W.A.$ changes also; we shall call such a system "osmotic variant".

This is the case f.i. with the systems:

$$Y + L_a, \quad Y + L_b, \quad Y + L_c \qquad \text{fig. 1, 2, 3 III}$$

$$H + L_c, \quad H + L_d \quad \text{fig. 1 IV;} \qquad H + L_a \quad \text{fig. 2 IV}$$

$$L_{a_1} + L_{a_3}, \quad L_{b_1} + L_{b_2}, \quad L_{c_2} + L_{c_3} \qquad \text{fig. 1, 2 XV.}$$

We now take two similar systems of such a composition that the one can arise from the other by taking in or losing water. This is f.i. the case with the systems $Y + L_b$ and $Y + L_c$ in fig. 1 III, if we choose the quantities of the phases in such a way that the points, which represent those two systems, are situated on a straight line going through point W.

If both systems, which we shall call E_1 and E_2, can be accidentally in equilibrium with one another, then they have the same $O.W.A.$ If this is not the case, then, if we bring both together, a new system E_3 will be formed. Consequently we have the conversion:

$$E_1 + E_2 \rightarrow E_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It now depends on the ratio of the quantities of E_1 and E_2 which system E_3 can be formed. If we take a definite ratio and if we consider stable states only, then E_3 is completely defined. If we now assume that E_1 has a greater amount of water than E_2, then appears from (1) that E_3

has also a greater amount of water than E_2 but smaller than E_1. Consequently we can have the conversions:

$$E_1 - water \rightarrow E_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$E_2 + water \rightarrow E_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We now form the osmotic system:

$$E_1 \,|\, E_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As herein by diffusion of water at both sides of the membrane the system E_3 can be formed, and as this system, as we assumed above, also is the most stable state, this will really take place. Therefore, as appears from (2) and (3) water must diffuse from E_1 to E_2. The O. W. A. of system E_2 (viz. of the system which has the smallest amount of water) is, therefore, greater than that of E_1.

We can apply those considerations also when one of the systems E_1 and E_2 or when both are osmotic invariant. Let us take f.i. the equilibria:

$$E_1 = H + Y + L_d \qquad E_2 = X + Y + L_c \quad \text{fig. 1 V.}$$

We imagine those equilibria to be represented by the points K_1 and K_2 (not drawn); consequently K_1 is situated within the triangle H Yd and K_2 within the triangle XYc of fig. 1 V. As E_2 passes into E_1 by taking in water, the points K_1 K_2 and W must be situated on a straight line. We now represent by K_3 the equilibrium E_3 which can be formed in accordance with reaction (1); this point K_3 is situated then anywhere on the line WK_1K_2 between K_1 and K_2; its place is defined by the ratio's of the quantities of E_1 and E_2 which we bring together. It now depends on the position of K_3 which equilibrium E_3 will arise. In accordance with the position of K_3 within the triangle HYd, the sector Ydc on the triangle XYc, E_3 is one of the equilibria:

$$H + Y + L_d \qquad Y + L \qquad X + Y + L_c \quad \text{fig. 1 V.}$$

The first of those equilibria is the same as E_1, with this difference, however, that the quantities of the phases are otherwise. The same is true for the last one, which is equal to E_2.

In similar way as above we now find that in (4) water must diffuse from E_1 towards E_2, so that the $O.W.A.$ of E_2 is greater than that of E_1.

We can apply similar considerations also to systems, in which one or more phases are the same (f.i. system $Y + D + L_c$ and $Y + D + X$ fig. 3 V), to systems which differ infinitely little in composition, etc. We now find:

Of two different stable systems, which can be converted into one another by taking in or losing water, and which are not in equilibrium with one another, the system with the smallest amount of water has the greatest $O.W.A.$

If in a stable equilibrium a phases-reaction occurs at taking in or

losing water, then it is osmotic invariant; its $O.W.A.$ viz. remains constant. If no phases-reaction occurs, then it is osmotic variant; its $O.W.A.$ becomes greater at losing water, and smaller at taking water in.

We now take the equilibrium

$$Y + L_b \quad \text{fig. 1 III}$$

which is represented in the figure by a point of the line bY f.i. point g. If we take away a little water from this system, then the liquid changes its composition; it shifts, starting from b along the saturation-curve in the direction towards v. As the $O.W.A.$ of the system increases at losing water, the $O.W.A.$ in the point b of the saturation-curve increases, therefore, in the direction of the arrow. If we apply this to all systems $Y + L$, in which L represents each liquid of the saturation-curve, then it appears, which we have already deduced previously in another way, that the $O.W.A.$ of the liquids of the saturation-curve increases in the direction of the arrows, viz. from w to v.

We find the same for the liquids of the saturation-curve in fig. 2 III; here also the $O.W.A.$ of the liquids increases in the direction from w towards v, notwithstanding the content of water of the liquids themselves firstly increases starting from w, in order to decrease later of course. It also appears in fig. 3 that the $O.W.A.$ increases in the direction of the arrows.

We now take the equilibria

$$H + L \quad \text{fig. 1 IV} \qquad D + L \quad \text{fig. 2 IV}$$

in which L represents an arbitrary liquid of the saturation-curve. In the same way as above we now find the property, already previously deduced, that the $O.W.A.$ increases from w to v.

In order to formulate this property in another way than formerly, we shall define the direction in which we move along a saturation-curve, in a corresponding way as in communication XIII for a binodalcurve. The line Yb (figs 1, 2 and 3 III) or Hb (fig. 1 IV) or Db (fig. 2 IV) divides the plane into two parts; in one of those parts the point W is situated. We now shall say that we go starting from b along the saturation-curve towards W, if we go along the saturation-curve towards that part of the plane, in which point W is situated. If we go in the other direction, then we shall say that we move away from the point W. We may summarize then the deduced above in the following way:

the $O.W.A.$ of the liquids of a saturation-curve increases in that direction, in which we move away along this curve from the point W.

Of course this rule is valid also, if the diffusing substance is other than water. If f.i. the substance Y diffuses, then we have to replace in the above rule $O.W.A.$ by $O.Y.A.$ and point W by point Y.

Let us take the figures of the communications XI and XII in which Y is the diffusing substance. We then find in accordance with previously

that the $O.W.A.$ along the saturation curve $a\,d\,g$ of the substance D (fig. 2 XI) must increase in the direction of the arrows. The same is true for the saturation-curve $a\,b$ of the substance H, for the saturation-curve $c\,d$ of the substance X and for the saturation-curve $f\,g$ of *Ice* in fig. 2 XII.

We can apply also the rule on the change of the $O.W.A.$ of an osmotic variant equilibrium to define the direction, in which the $O.W.A.$ of the liquids of a binodal-curve increases. Let us take f.i. the equilibrium:

$$L_{a_1} + L_{a_2} \quad \text{fig. } 1-3 \text{ XIII.}$$

If we take away from this system a little water, then those liquids shift along the binodal-curve away from the point W; consequently they move in the direction of the arrows. Those arrows, therefore, indicate also the direction, in which the $O.W.A.$ increases. In accordance with previously we find, therefore:

the $O.W.A.$ of the liquids of a binodal-curve increases in that direction in which we move away along this curve from the point W.

Consequently this rule is the same as that for the saturation-curve of a solid substance; the only difference is, that with the saturation-curve the conjugation-line solid-liquid, and with the binodal-curve the conjugation-line of two coexisting liquids plays a part.

We now take the equilibrium

$$E = L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. } 1 \text{ XV} \quad \ldots \quad \ldots \quad (5)$$

When taking in water, herein occurs, as appears from the figure, the reaction:

$$L_{q_3} + water \rightarrow L_{q_1} + L_{q_2} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$
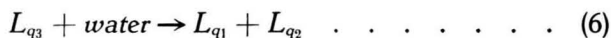
The quantity of the liquid q_3 decreases, therefore, that of the liquids q_1 and q_2 increases; with sufficient taking water in arises, therefore, the equilibrium $L_{q_1} + L_{q_2}$, which passes into an equilibrium $L(q_1 b_1) + L(q_2 b_2)$ by taking further water in. Herein $L(q_1\,b_1)$ represents a liquid of curve $q_1\,b_1$ and $L(q_2 b_2)$ a liquid of curve $q_2\,b_2$. As this equilibrium arises from (5) by taking water in, it has, therefore, a smaller $O.W.A.$ than system (5). This is in accordance with the direction of the arrows on the binodal-curve $q_1\,{}^a q_2$.
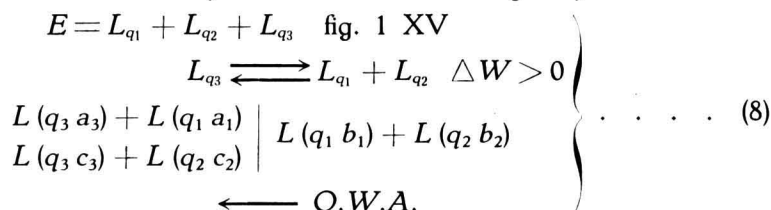
At losing water in the system (5) occurs the reaction:

$$L_{q_1} + L_{q_2} - water \rightarrow L_{q_3}; \quad \ldots \quad \ldots \quad \ldots \quad (7)$$
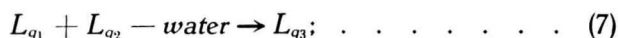
with sufficient loss of water arises, therefore, one of the systems: $L_{q_1} + L_{q_3}$ or $L_{q_2} + L_{q_3}$. It depends on the ratio of the quantities of L_{q_1} and L_{q_2} in (5) which of those systems arises in a special case. With further loss of water arises one of the systems: $L(q_1\,a_1) + L(q_3\,a_3)$ or $L(q_2\,c_2) + L(q_3\,c_3)$ in which are indicated again between parentheses the curves on which the liquids are situated. As those equilibria arise from
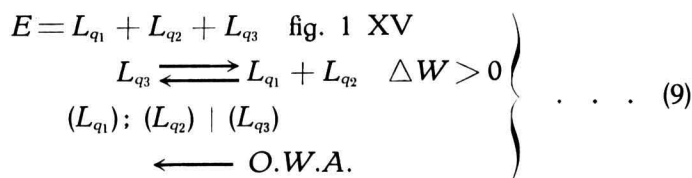
(5) by losing water, they have a greater $O.W.A.$ than system (5); this is in accordance with the direction of the arrows in the figure.

We shall summarize the previous in the following way:

$$\left.\begin{array}{l} E = L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. 1 XV} \\ \qquad L_{q_3} \rightleftharpoons L_{q_1} + L_{q_2} \quad \triangle W > 0 \\ \begin{array}{l} L(q_3\,a_3) + L(q_1\,a_1) \\ L(q_3\,c_3) + L(q_2\,c_2) \end{array} \Big| \ L(q_1\,b_1) + L(q_2\,b_2) \\ \qquad\qquad \longleftarrow O.W.A. \end{array}\right\} \quad \cdots \quad (8)$$

In the first line of (8) we find the osmotic invariant system, in the second the reaction which occurs between the phases at taking in and losing water. On the right side of this reaction we still find $\triangle W > 0$; this means that the reaction takes place from left to right with taking in water. In accordance with this we find at the right side of the vertical line the equilibrium, which is formed with taking in water, at the left side of this line the equilibria which are formed with loss of water. Consequently the equilibria at the left side of this line have a larger $O.W.A.$ than the equilibrium E, those at the right side of the line have a smaller $O.W.A.$ This is indicated by the direction of the lowest arrow.

We shall represent by (L_{q_3}) the equilibrium $L(q_1 b_1) + L(q_2 b_2)$, which is formed from E, when herein disappears the phase L_{q_3}; the equilibrium $L(q_3 a_3) + L(q_1 a_1)$ which is formed from E, when herein the phase L_{q_2} disappears, is represented by (L_{q_2}) and the equilibrium $L(q_3 c_3) + L(q_2 c_2)$ which is formed from E, when herein the phase L_{q_1} disappears, by (L_{q_1}). Instead of (8) we may write then:
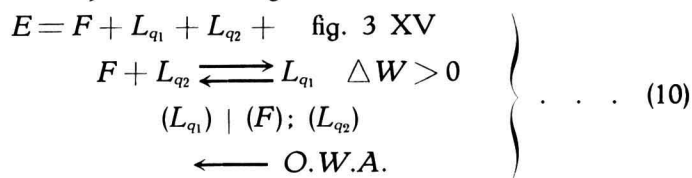
$$\left.\begin{array}{l} E = L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. 1 XV} \\ \qquad L_{q_3} \rightleftharpoons L_{q_1} + L_{q_2} \quad \triangle W > 0 \\ (L_{q_1}); \ (L_{q_2}) \mid (L_{q_3}) \\ \qquad\qquad \longleftarrow O.W.A. \end{array}\right\} \quad \cdots \quad (9)$$

For the equilibrium of the three liquids in fig. 2. XV is the reaction:

$$L_{q_1} + L_{q_2} \rightleftarrows L_{q_3} \qquad \triangle W > 0.$$
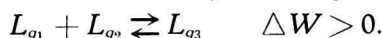
In (9) we have, therefore, to replace by one another the systems at the right and at the left of the vertical line. This is also in accordance with the direction of the arrows in this figure.

For the threephases-equilibrium of fig. 3. XV is found:

$$\left.\begin{array}{l} E = F + L_{q_1} + L_{q_2} + \quad \text{fig. 3 XV} \\ \qquad F + L_{q_2} \rightleftharpoons L_{q_1} \quad \triangle W > 0 \\ (L_{q_1}) \mid (F); \ (L_{q_2}) \\ \qquad\qquad \longleftarrow O.W.A. \end{array}\right\} \quad \cdots \quad (10)$$

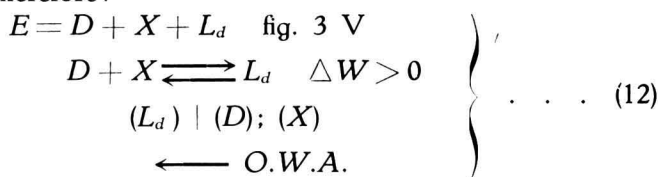Herein (L_{q_1}) represents the equilibrium, which arises from E, if the

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liquid L_{q_1} disappears from this; consequently we have: $(L_{q_1}) = F + L$, in which L is a liquid of curve $q_2 f$. In accordance with (10) the $O.W.A.$ of this system must be larger than that of equilibrium E; this is in accordance with the direction of the arrow on curve $d_2 f$ of the figure.

(F) represents the system, which arises from E if the substance F disappears from this, consequently two conjugated liquids of the binodal-curve $q_1 \alpha q_2$; in accordance with (10) the $O.W.A.$ of this system is smaller than that of the equilibrium E; the same is true for the equilibrium $(L_{q_2}) = F + L$, in which L represents a liquid of curve $q_1 w$.

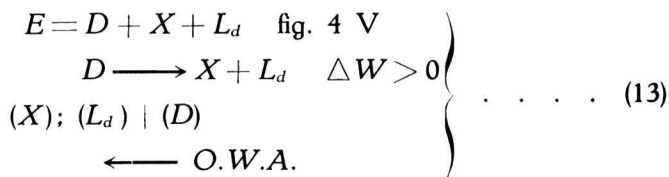In the equilibrium $D + X + L_d$ of fig. 3. V occurs the reaction:

$$D + X \rightleftarrows L_d \qquad \triangle W > 0 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

We may write, therefore:

$$\left. \begin{array}{c} E = D + X + L_d \quad \text{fig. 3 V} \\ D + X \rightleftarrows L_d \quad \triangle W > 0 \\ (L_d) \mid (D); (X) \\ \longleftarrow O.W.A. \end{array} \right\} \quad . \quad . \quad . \quad (12)$$

The equilibria $(D) = X + L$ and $(X) = D + L$ have, therefore, a smaller $O.W.A.$ than the equilibrium E; the direction of the arrows on the curves db and ds is in accordance with this. As (L_d) represents the equilibrium which is formed from E by loss of water, we may have, in accordance with the figure: $(L_d) = D + X + Y$. The $O.W.A.$ of this system is larger, therefore, than that of the system E. We have already deduced this in another way in communication VI.

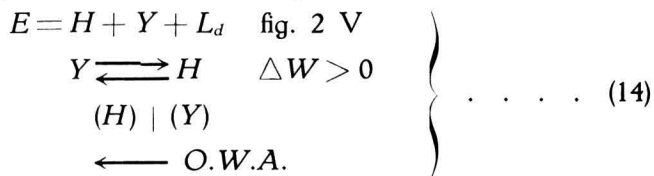We now take the same threephases-equilibrium as in (12), but now in fig. 4. V. We then find:

$$\left. \begin{array}{c} E = D + X + L_d \quad \text{fig. 4 V} \\ D \longrightarrow X + L_d \quad \triangle W > 0 \\ (X); (L_d) \mid (D) \\ \longleftarrow O.W.A. \end{array} \right\} \quad . \quad . \quad . \quad (13)$$

The equilibrium $(X) = D + L$ is situated now on the other side of the vertical line than in (12); therefore, the $O.W.A.$ must increase along the saturation-curve of D in fig. 4. V starting from the point d.

In the equilibrium $E = H + Y + L_d$ of fig. 2. V occurs the reaction:

$$Y \rightleftarrows H \qquad \triangle W > 0.$$

As the liquid does not take part in the reaction we may call E a singular equilibrium [1]) and L_d its indifferent phase. We now find:

$$\left. \begin{array}{c} E = H + Y + L_d \quad \text{fig. 2 V} \\ Y \rightleftarrows H \qquad \triangle W > 0 \\ (H) \mid (Y) \\ \longleftarrow O.W.A. \end{array} \right\} \quad . \quad . \quad . \quad (14)$$

[1]) F. A. H. SCHREINEMAKERS, In-, mono- and plurivariant equilibria XXVII and XXVIII.

In accordance with the arrows in fig. 2, V it follows from this that $(H) = Y + L$ has a greater and $(Y) = H + L$ has a smaller $O.W.A.$ than the system E.

If we introduce a semi-permeable membrane in an equilibrium E then it does not change its stability, we then get an osmotic equilibrium:

$$E_1 \,|\, E_2 \qquad \ldots \ldots \ldots \ldots \quad (15)$$

If we represent the thermodynamical potential of the system E by Z, then, if this system contains one or more phases, which change their composition at taking in or losing water, and if E_1 and E_2 each contain the half of the phases of system E, at diffusion of δn quantities of water the thermodynamical potential at the one side of the membrane will become:

$$\frac{1}{2} \left[Z + \frac{\partial Z}{\partial n} \cdot \delta n + \frac{1}{2} \cdot \frac{\partial^2 Z}{\partial n^2} \cdot \partial n^2 + \ldots \right]$$

and at the other side:

$$\frac{1}{2} \left[Z - \frac{\partial Z}{\partial n} \cdot \delta n + \frac{1}{2} \cdot \frac{\partial^2 Z}{\partial n^2} \cdot \partial n^2 - \ldots \right].$$

Consequently the total thermodynamical potential becomes:

$$Z + \frac{1}{2} \frac{\partial^2 Z}{\partial n^2} \cdot \partial n^2 + \ldots \quad , \quad . \quad , \quad . \quad . \quad . \quad . \quad (16)$$

If we assume that system E and, therefore, also the osmotic system (15) is stable for small disturbances of equilibrium, then (16) must be greater than Z, so that $\frac{\partial^2 Z}{\partial n^2}$ is positive. As $\frac{\partial Z}{\partial n} = \varphi, \frac{\partial \varphi}{\partial n}$ must be positive, therefore. Consequently the φ of system E increases at taking in a little water. Hence follows the rule, already deduced above:

the $O.W.A.$ of a stable osmotic variant equilibrium becomes greater when losing water and smaller when taking water in.

This rule needs however to be true no more for systems, which are unstable for small changes of equilibrium. Let us imagine in a diagram f. i. in fig. 1 XIV a straight line to be drawn through point W. We take on this line a point Q and we represent the composition of a liquid L by:

x quant. of $W + y$ quant. of $N + (1-x-y)$ quant. of Q

in which N is an arbitrary phase. The $O.W.A.$ of this liquid L is defined by:

$$\varphi = \zeta + (1-x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \qquad \ldots \ldots \quad (17)$$

For a new liquid L', which differs infinitely little from L, is true, therefore:

$$d\varphi = [(1-x)\, r - ys]\, dx + [(1-x)\, s - yt]\, dy \quad . \quad . \quad . \quad (18)$$

If we imagine the liquid L to be in the point Q and the new liquid L' on the line WQ (so that $dy = 0$) then (18) passes into:

$$d\varphi = r\,dx \qquad \ldots \ldots \ldots \quad (19)$$

Wo now go in fig. 1 XIV f.i. along the line Wb from the liquid L towards the new liquid L', which is situated somewhat further from point W. As then dx is negative and r is positive in all points of this line $d\varphi$ is negative, therefore. The same is true of course for all liquids of the parts of a straight line going through point W, which are situated outside the region of dimixtion. Consequently we find in accordance with previously:

the $O.W.A.$ of a stable liquid becomes greater when losing water and smaller when taking water in.

Otherwise it is, however, if we take a liquid which is situated within the spinodalcurve (and, therefore, surely within the region of dimixtion); then r can be negative. If we take f.i. the line Wu of fig. 1 XIV; previously we have assumed that r in the points c and m is zero, and negative between these points. In connection with this an isotonic curve touches this line Wu in c and an other curve (not drawn) touches it in m. It now follows from (19):

the $O.W.A.$ of a liquid between c and m (fig. 1 XIV) becomes smaller when losing water and greater when taking water in.

We see this also from the figure, if we imagine to be drawn in this still some isotonic curves, situated between the two, which touch in c and m the line Wu.

Also the rule, deduced above, that the $O.W.A.$ of the liquids of a saturation-curve increases in that direction in which we move along this curve from the point W, needs to be true no more when the system is unstable for small changes in equilibrium. Let us take f.i. the saturation-curve $a\,q_1\,q_2\,f$ of the substance F in fig. 3 XV. It appears from the direction of the arrows that the rule above mentioned is not valid for the parts $l\,m$ and $p\,n$ of this curve, which are situated within the region of dimixtion, but it is valid for the parts $q_1\,l$, $m\,n$ and $p\,q_2$ which are situated also within the region of dimixtion.

(To be continued.)