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

(Communicated at the meeting of February 27, 1926).

Ternary systems in which dimixtion into two and three liquids occurs.

We now shall consider the case that also three liquids can be in equilibrium with one another. In the figures 1 and 2 in which only the angle-point W of the components-triangle is drawn, $q_1 q_2$ and q_3 represent the three liquids being in equilibrium with one another. As each point within the triangle $q_1 q_2 q_3$ represents a complex of those three liquids, we may call therefore, triangle $q_1 q_2 q_3$ also the region of dimixtion of three liquids.

At each side of triangle $q_1 q_2 q_3$ joins a region of dimixtion of two liquids; consequently there are three of those regions of dimixtion and also, therefore, three binodalcurves. In fig. 1 on the binodalcurve $q_1 a q_2$ a critical liquid a is drawn.

The branches of the binodalcurves are drawn in the figures, as if they terminate in the points $q_1 q_2$ and q_3; this is, however, not the case, they continue viz. within the region of dimixtion [1]). If we limit ourselves to stable states, then we may leave out of consideration those parts, situated within the region of dimixtion, which represent only metastable and unstable states.

For the position of two binodalcurves in the vicinity of their point of intersection is true:

both curves are situated either both within the conjugation-angle or both within the supplement-angle; if the one curve touches the one leg, then the other curve touches the other leg.

As liquid q_1 can be in equilibrium with the liquids q_2 and q_3, angle $q_2 q_1 q_3$ (and its opposite angle) is the conjugation-angle in point q_1. The two binodalcurves are drawn in the vicinity of q_1 (figs 1 and 3) within the supplement-angle; this is also the case in the other points q_2 and q_3 of those figures, excepted in the point q_3 of fig. 2 in which both curves are situated within the conjugation-angle $q_1 q_2 q_3$.

In the previous communication we have deduced:

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[1]) For considerations more in detail compare: F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. Drittes Heft; Zweiter Teil, pg. 297 and following, figs. 120—124.

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

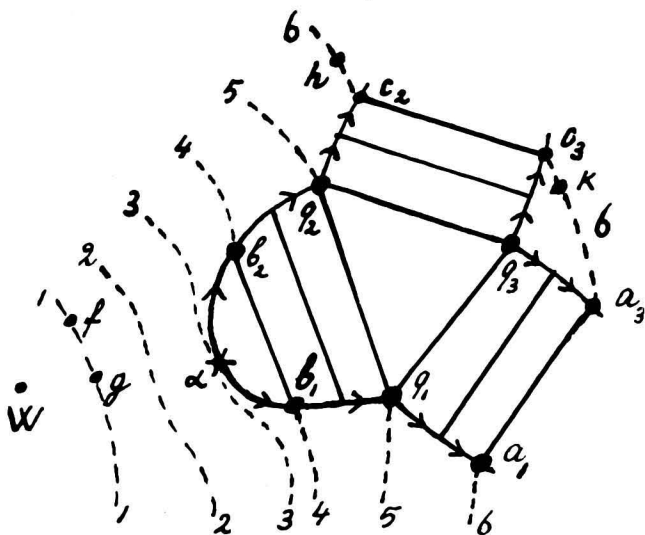If we apply this rule to the binodalcurve q_1 a q_2 (fig. 1), then follows that the $O.W.A.$ of the liquids must increase starting from a towards q_1 and q_2, consequently in the direction of the arrows; it follows for the branches $q_2 c_2$ and $q_3 c_3$ that the $O.W.A.$ increases starting from q_2 towards c_2 and starting from q_3 towards c_3 and for the branches $q_3 a_3$ and $q_1 a_1$ starting from q_3 and q_1 towards a_3 and a_1. If we apply this rule also to the binodalcurves of fig.

Fig. 1.

2, then we see that the arrows in both figures indicate the direction in which the $O.W.A.$ increases along the binodalcurve.

The dotted curves of those figures represent isotonic curves; they are only drawn so far as they represent stable states and are situated, therefore, out of the region of dimixtion. In the previous communications we have discussed already the parts of those curves situated within the region of dimixtion and we have also deduced the conditions which must be satisfied by binodalcurves and isotonic curves in the vicinity of their point of intersection.

Let us firstly consider fig. 1. The isotonic curve 3, which touches the binodalcurve in the critical point a, is curved in this point in the same direction as the binodalcurve; the isotonic curve 4 consists of two branches, which are united with one another by the conjugationline $b_1 b_2$. As the liquids q_1, q_2 and q_3 can be in equilibrium with one another and have, therefore, also the same $O.W.A.$, the isotonic curve 5 consists still also of the isolated point q_3 besides of the two branches, which are united by the conjugationline $q_1 q_2$. Consequently all liquids of curve (5) have the same $O.W.A.$ as liquid q_3. If we represent an arbitrary liquid of curve 5 by L_5, then we can have, therefore, the osmotic equilibrium:

$$L_5 \,|\, L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. 1.}$$

Of course herewith it is immaterial which is the ratio of the quantities of the liquids at the right side of the membrane and whether one or two of those are totally failing.

The isotonic curve 6 consists of three branches, which are united with one another by the conjugation-lines $c_2 c_3$ and $a_1 a_3$. If we represent a liquid of curve 6 by L_6, we can have a.o. the following osmotic equilibria:

$$L_6 \,|\, L_{c_2} + L_{c_3} \qquad L_6 \,|\, L_{a_1} + L_{a_3} \qquad L_{a_1} + L_{a_3} \,|\, L_{c_2} + L_{c_3} \qquad \text{fig. 1.}$$

Of the many phenomena, which may occur in osmotic systems, we only shall discuss a few of them.

Let us take the osmotic system:

$$L \xrightarrow{\;|\;} L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad (1)$$
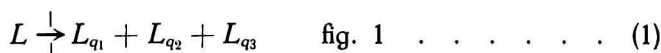
in which L represents a liquid, which is situated at the same side of curve 5 and the line $q_1 q_2$ as point W. As, therefore, the $O.W.A.$ of the system at the right side of the membrane is larger than that of the liquid L, the water in (1) diffuses, therefore, from left towards right, as is indicated by the arrow. Consequently, in the system at the right side of the membrane, as appears at once from fig. 1, the reaction:

$$water + L_{q_3} \rightarrow L_{q_1} + L_{q_2} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad (2)$$

occurs, so that the quantity of the liquids q_1 and q_2 increases, but that of q_3 decreases. We now assume that so much of the liquid q_3 is present, that the system at the right side of the membrane remains. Then it depends on the composition of liquid L, which osmotic equilibrium will be formed from (1). If we take f.i. the liquid f then (1) passes into:

$$L'_f \,|\, L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad (3)$$
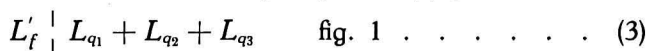
in which L'_f is the point of intersection of the line Wf with the isotonic curve (5). If we take in (1) for L f.i. the liquid g or the critical liquid a or a complex of the liquids b_1 and b_2, then is formed at the left side of the membrane the same system as at the right side, or the system $L_{q_1} + L_{q_2}$.

We now take a liquid L which is situated at the other side of curve 5 and the lines $q_1 q_3$ and $q_2 q_3$ than point W. As the $O.W.A.$ of this liquid is greater now than that of the complex of the three liquids, we now have, therefore, an osmotic system:

$$L \xleftarrow{\;|\;} L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$
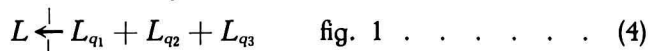
in which water diffuses from right to left. At the right side of the membrane then occurs the reaction:

$$L_{q_1} + L_{q_2} - water \rightarrow L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad (5)$$

so that the quantity of liquid q_3 increases, and that of q_1 and q_2 decreases. We now assume that there is present so much of the liquids q_1 and q_2, that the system at the right side of the membrane remains. If we take in (4) for L f.i. the liquid L_h, then is formed the osmotic equilibrium:

$$L'_h \,|\, L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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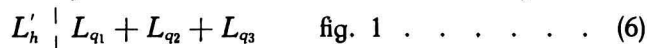
in which L^1_h is represented by the point of intersection of the line Wh with curve 5. If we take in (4) for L the liquid K then is formed at the left side of the membrane the same system as at the right side or the system $L_{q_2} + L_{q_3}$.

Let us take once more the osmotic system:

$$L_f \xrightarrow{|} L_{q_1} + L_{q_2} + L_{q_3} \qquad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad (7)$$
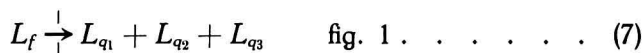
in which the water diffuses in the direction of the arrow, so that at the right side of the membrane reaction (2) takes place. If no sufficient quantity of the liquid q_3 is present, so that this disappears totally, then it depends on the ratio of the quantities of the liquids which osmotic equilibrium will be formed. We imagine the complex of the three liquids at the right side of the membrane to be represented by a point Q (not drawn) which is situated anywhere within the triangle $q_1 q_2 q_3$. The complex of the total system (7) is represented then by a point R (not drawn) which is situated anywhere on the line fQ. The position of the point R now defines on which isotonic curve the osmotic equilibrium which must arise from (7) will be formed. If this is the case f.i. on the isotonic curve (2) then arises the osmotic equilibrium:

$$L'_f \mid L'_Q$$
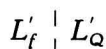
in which L'_f and L'_Q represent the points of intersection of the lines Wf and WQ with curve 2. If the equilibrium is formed on the isotonic curve 3, then L'_f and L'_Q represent the points of intersection of the lines Wf and WQ with curve 3. If it is formed on the isotonic curve 4, then may arise the osmotic equilibrium

$$L'_f \mid L_{b_1} + L_{b_2} \qquad \text{fig. 1}$$
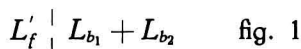
in which L'_f is the point of intersection of the line Wf with curve 4. The ratio of the quantities of both liquids at the right side of the membrane is defined by the point of intersection of the lines WQ and $q_1 q_2$.
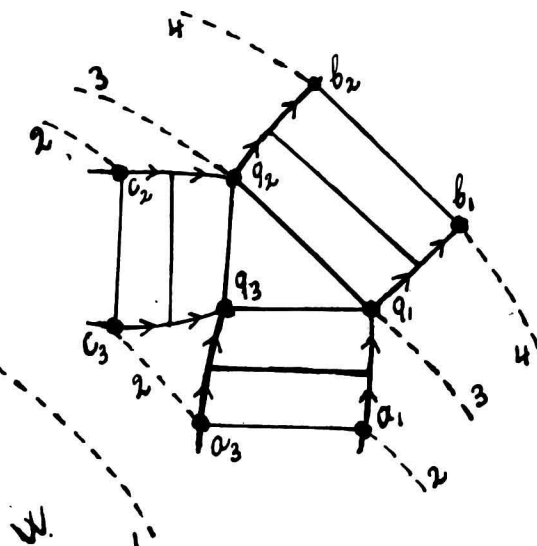

Fig. 2.

We now take fig. 2. The isotonic curve 2 consists of three branches, which are united by the conjugation-lines $a_1 a_3$ and $c_2 c_3$; the isotonic curve 3 consists, besides of two branches, which are united with one

another by the conjugation-line $q_1 q_2$, still also of the isolated point q_3; the isotonic curve 4 consists of the two branches, united by the conjugation-line $q_1 q_2$.

We now consider the osmotic system:

$$L \mid L_{q1} + L_{q2} + L_{q3} \qquad \text{fig. 2} \quad . \quad . \quad . \quad . \quad (8)$$
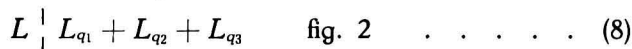
If herein L represents a liquid or a complex of two liquids, which is situated on the same side of curve 3 and the lines $q_1 q_3$ and $q_2 q_3$ as the point W, then L has a smaller O.W.A. than the system of the three liquids. In (8) water diffuses, therefore, from left to right. It appears from fig. 2 that then at the right side of the membrane the reaction:

$$L_{q1} + L_{q2} + water \rightarrow L_{q3} \qquad \text{fig. 2} \quad . \quad . \quad . \quad . \quad (9)$$

occurs. If L is situated in (8) at the other side of curve 3 and the line $q_1 q_2$ than the point W, then the water in (8) diffuses from right to left. Then at the right side of the membrane the reaction:

$$L_{q3} - water \rightarrow L_{q1} + L_{q2} \qquad \text{fig. 2} \quad . \quad . \quad . \quad . \quad (10)$$

occurs. The reader now can easily deduce the osmotic equilibria, which may be formed from system (8) and other osmotic systems of fig. 2.

If we compare the figs 1 and 2 with one another, then we see that in both three regions of dimixtion of two liquids join at the region of dimixtion $q_1 q_2 q_3$ of three liquids.

Starting from the region of dimixtion of the three liquids in fig. 1 the O.W.A. increases along two of the binodalcurves and it decreases along the third, in fig. 2, however, the O.W.A. decreases along two of the binodalcurves and it increases along the third.

One could still imagine two other cases viz. that the O.W.A. either increases or decreases along each of the three binodalcurves; this is impossible, however. If we consider viz. the position of point W and of triangle $q_1 q_2 q_3$ with respect to one another, then we find only the two cases, represented by figs 1 and 2. As long as we assume viz. that the diffusing substance W is a component, point W cannot be situated within the triangle $q_1 q_2 q_3$. We shall refer to this later.

The change of the O.W.A. of the liquids of a saturation-curve of a solid substance.

In the communications III and IV we have deduced a rule for the change of the O.W.A. of the liquids of a saturation-curve. We found that the O.W.A. in the figs 1, 2 and 3 (Comm. III) in which $w v$ represents the saturation-curve of the solid component Y, increases in the direction of the arrows viz. from w towards v. The same is true for curve $w v$ which represents in fig. 1 IV the saturation-curve of a hydrate H and for curve $w v$, which represents in fig 2 IV the saturation-curve of a ternary compound F. If the diffusing substance is

another than water, as f. i. the component Y in the figures of the com-
munication XI and XII, then a corresponding rule is valid.

In fig. 3 (of this communication) $a\,q_1$ and $q_1\,f$ represent two parts of
the saturation-curve of the substance F. This curve intersects the binodal-
curve $q_1\,\alpha\,q_2$ in the two conjugated points q_1 and q_2 so that also an
equilibrium:

$$F + L_{q_1} + L_{q_2} \qquad \text{fig. 3}$$

can exist. Of course the saturation-curve does not finish in q_1 and q_2,
but it passes through the region of dimixtion. If the saturation- and the
binodal-curve intersect one another only in two points, then it goes, as
is indicated in the figure by the dotted curve $q_1\,m\,n\,q_2$, from q_1 towards
q_2 [1]). This part, situated within the region of di-
mixtion represents only metastable and unstable states.
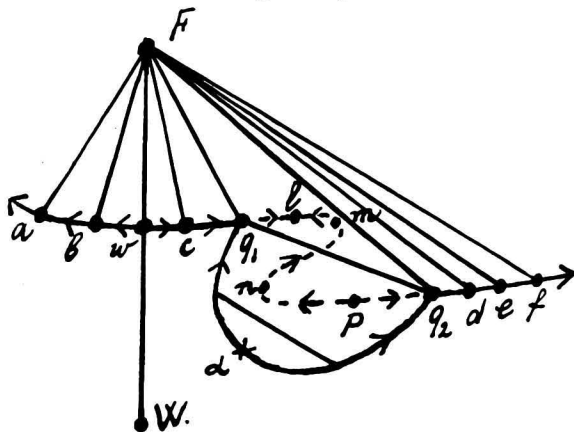
Figuur 3.

The rule, mentioned above, for the change of the $O.W.A.$ of the liquids of a saturation-curve is true only for stable states, consequently in fig. 3 for the parts $a\,q_1$ and $q_2\,f$. On those parts the $O.W.A.$ must increase, there-
fore, from w towards a and towards q_1 and from q_2 towards f. As q_1
and q_2 are conjugated liquids and have, therefore, the same $O.W.A.$,
it appears, also from this at once that the rule above-mentioned cannot
be valid for the part $q_1\,m\,n\,q_2$. In order to examine this more in detail,
we represent the composition of an arbitrary liquid L by:

$$x \text{ quant. } W + y \text{ quant. } F + (1-x-y) \text{ quant. } N \quad . \quad . \quad . \quad (11)$$

in which N is an arbitrary liquid of the saturation-curve. It is clear,
however, that we are not allowed to take for N the liquid w or a
liquid in the immediate vicinity. Consequently we have a system of
coordinates with the point N as origin, the line NW as X-axis and
NF as Y-axis.

If the liquid L defined by (11) is saturated with the solid substance
F, then is satisfied:

$$\zeta - x\frac{\partial \zeta}{\partial x} + (1-y)\frac{\partial \zeta}{\partial y} = \zeta_F \quad . \quad . \quad . \quad . \quad . \quad (12)$$

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[1]) For the case there are more points of intersection, compare F. A. H. SCHREINEMAKERS
l.c., figs. 136—139. Examples of similar diagrams are found in the system: water +
phenol + anilin.

while the $O.W.A.$ of this liquid is defined by:

$$\varphi = \zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

With the aid of (12) we can also write for this:

$$\varphi = \frac{\partial \zeta}{\partial x} - \frac{\partial \zeta}{\partial y} + \zeta_F \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

For a liquid; which differs infinitely little from L, are valid, therefore:

$$[-xr + (1-y)s]\,dx + [-xs + (1-y)\,t]\,dy + A = 0 \quad . \quad . \quad (15)$$

$$\triangle \varphi = (r-s)\,dx + (s-t)\,dy + B . \quad . \quad . \quad . \quad . \quad (16)$$

in which A and B contain terms of higher order. If liquid L coincides with the point N, so that $x = 0$ and $y = 0$, then they pass into:

$$s\,dx + t\,dy + A_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\triangle \varphi = (r-s)\,dx + (s-t)\,dy + B_0 \quad . \quad . \quad . \quad . \quad (18)$$

so that we may write for (18) also

$$\triangle \varphi = r\,dx + s\,dy + A_0 + B_0 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Limiting ourselves to magnitudes of the first order, then follows from (17) and (19):

$$\frac{dy}{dx} = -\frac{s}{t} \quad . \quad . \quad . \quad . \quad (20^a) \qquad \triangle \varphi \doteq \frac{rt-s^2}{t}\,dx \quad . \quad . \quad . \quad (20^b)$$

The equations (17) and (19) and consequently also (20^a) and (20^b) define the direction of the saturation-curve and the change of the $O.W.A.$ in each arbitrary point (excepted in the vicinity of the point w).

We now take an arbitrary point of the saturation-curve outside the region of dimixtion f. i. the point b. As t is positive in this point, $s:t$ can never be infinitely large, therefore; it now follows from (20^a) that the saturation-curve in b cannot touch the Y-axis, viz. the line bF.

If we take dx positive, then we go along the curve from b towards w; if we take dx negative, then we go from b towards a. As the coefficient of dx in (20^b) is positive, it follows that φ decreases starting from b towards a, so that the $O.W.A.$ increases from b to a. If we apply this same to other points of the saturation-curve situated outside the region of dimixtion, then we see that the $O.W.A.$ increases in the direction of the arrows, viz. in that direction, in which we move away from the point w along the saturation-curve.

If we go along the saturation-curve from q_1 towards q_2 then we intersect the spinodal-curve in the two points l and p, in which, therefore, $rt - s^2 = 0$. In accordance with (20^a) the saturation-curve shows nothing particular in those points. In accordance with (20^b) the change of the $O.W.A.$ is zero in those points, however, and the $O.W.A.$ itself a maximum or minimum, therefore.

If we go from l towards p, then t

1. can remain always positive
2. become zero in the points m and n. As t is zero in those points, $rt - s^2$ is negative; consequently the points m and n are situated within the spinodal-curve, the same as the part mn, on which t is negative.

As $s:t$ in the points m and n becomes infinitely large, it follows from (20ª) that the saturation-curve touches in those points the lines mF and nF. Those tangents, situated always within the region of dimixtion, are the only ones which can be drawn from F to the saturation-curve. If t is positive in all points between l and p, then those tangents mF and nF fall away also and the retracing part mn of the curve.

It now follows from the previous:

the $O.W.A.$ increases from q_1 to l, it decreases from l to p and it increases again from p to q_2 in order to become in q_2 the same again as in q_1. In the one point of intersection with the spinodal-curve the $O.W.A.$ is maximum, in the other it is a minimum. The isotonic curves going through the points l and p must touch, therefore, the saturation-curve in those points.

The latter appears still also in the following way. In the previous communication we have seen that an isotonic W-curve is defined in every point by:

$$\frac{dy}{dx} = -\frac{r}{s} \qquad \ldots \ldots \ldots \ldots (21)$$

As $rt - s^2$ is zero in the points l and p, it follows that (20ª) and (21) have the same value, so that isotonic curve and saturation-curve touch one another.

In order to define the change of the $O.W.A.$ in the vicinity of the point w (fig. 3) we might take the liquid w as fundamental composant; for the two other composants we can choose F (or W) and an arbitrary other phase. We shall keep, however, the same composants as above; for the liquid w is then true: $x + y = 1$.

Substituting in (15) $x = 1 - y$ then follows for (16):

$$(1-y) \triangle \varphi = A + (1-y) B \qquad \ldots \ldots \ldots (22)$$

As A and B contain only terms of higher order than the first, $\triangle \varphi$ is zero at first approximation. Consequently the $O.W.A.$ is in w a maximum or minimum. In order to examine this more in detail, we write for A the terms of the second order and put herein also $x = 1 - y$. We then find:

$$A = \frac{1}{2}\left[-r-(1-y)\left(\frac{\partial r}{dx}-\frac{\partial s}{\partial x}\right)\right]dx^2 + \left[-s-(1-y)\left(\frac{\partial r}{dy}-\frac{\partial s}{\partial y}\right)\right]dx\,dy +$$
$$+ \frac{1}{2}\left[-t-(1-y)\left(\frac{\partial s}{\partial y}-\frac{\partial t}{\partial y}\right)\right]dy^2.$$

It follows for B:

$$B = \frac{1}{2}\left(\frac{\partial r}{\partial x} - \frac{\partial s}{\partial x}\right) dx^2 + \left(\frac{\partial r}{\partial y} - \frac{\partial s}{\partial y}\right) dx\, dy + \frac{1}{2}\left(\frac{\partial s}{\partial y} - \frac{\partial t}{\partial y}\right) dy^2$$

so that (22) passes into:

$$(1-y)\, \triangle\varphi = \left(\frac{1}{2}\, r\, dx^2 + s\, dx\, dy + \frac{1}{2}\, t\, dy^2\right) . \quad . \quad . \quad . \quad (23)$$

If the point w is situated out of the region of dimixtion, the second part of (23) is always negative. If, as in fig. 3, the point w is situated between W and F then $1-y$ is positive. Consequently $\triangle\varphi$ is negative, φ is a maximum, therefore, and the $O.W.A.$ in w a minimum. If w is situated at the other side of point F as f. i. point v in fig. 2 IV, then $1-y$ is negative; the $O.W.A.$ is then a maximum in this point.

(To be continued).