Chemistry. — *Osmosis of ternary liquids. General considerations VIII.*
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Isotonic- and isentonic W-curves.

We take an osmotic system

$$g \mid L \quad \ldots \ldots \ldots \ldots \quad (1)$$

in which on the left side of the membrane a liquid, which has been represented in fig. 1 by point g. Now we may put among other things the questions :

1. which liquids have the same O.W.A. as liquid g?
2. which liquids have the same O.W.n.A. as liquid g?

In the preceding communication we have seen :

all liquids, which have the same O.W.A. as liquid g are situated on the isotonic W-curve, running through point g. This has been represented in fig. 1 by the dotted curve a f g h b ;

all liquids, which have the same O.W.n.A. as liquid g are situated on the isentonic W-curve, running through point g. This has been represented in fig. 1 by $p\,q\,g\,r\,s$.

Generally the two curves are different ; the form of the isotonic curve namely depends on the nature of the liquids only ; the form of the isentonic curve, however, depends not only on the nature of the liquids but also on the nature of the membrane $M\,(n)$ and, therefore, differs with different membranes.

In system (1) we put a membrane $M\,(W)$ viz. a membrane, which is only permeable for W (*water*) ; we represent this system by :

$$g \mid M(W) \mid L \quad \ldots \ldots \ldots \ldots \quad (2)$$

If herein L is a liquid of the isotonic W-curve $a\,g\,b$, then in this system no W will pass through the membrane $M\,(W)$.

If we put in (1) a membrane $M\,(n)$, viz. a membrane, which is permeable for all substances, we have the system :

$$g \mid M(n) \mid L \quad \ldots \ldots \ldots \ldots \quad (3)$$

If herein L is a liquid of the isentonic W-curve $p\,g\,s$, then in this system no W will pass through the membrane $M\,(n)$.

In Gen. VI we have seen already that there exist an infinite number of isotonic W-curves ; there exist also an infinite number of isentonic

W-curves; in fig. 1 three of them have been drawn, viz. $p_1 s_1$, $p s$ and $p_2 s_2$. All liquids of $p_1 s_1$ have the same O.W.n.A., also all liquids of $p s$ and in the same way those of $p_2 s_2$. The O.W.n.A. of the liquids of curve $p_1 s_1$, however, differs from that of the liquids of $p s$ and their O.W.n.A. is different again from that of the liquids of $p_2 s_2$.

In Gen VI we have deduced some properties of isotonic curves, among others:

two isotonic curves can cut nor touch one another;

the O.W.A. of the liquids of an isotonic W-curve is greater (smaller) the farther (closer) this curve is situated from (to) point W.

If in fig. 1 we imagine the isotonic W-curves drawn through e, q and d,

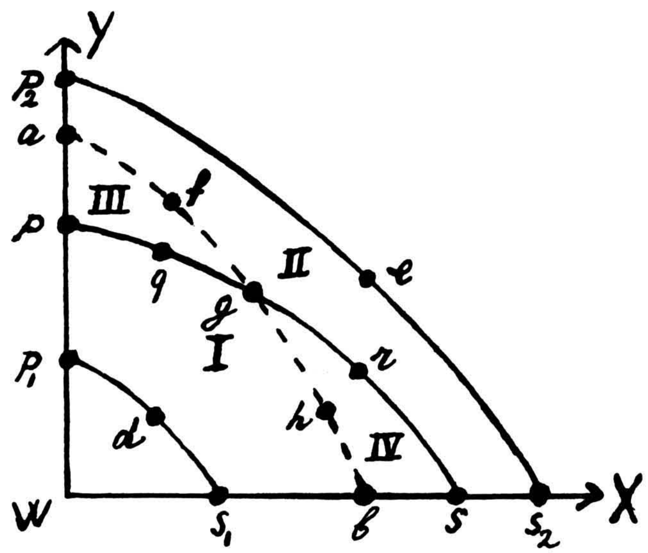

Fig. 1.

we see that liquid e has a greater, but q and d have a smaller O.W.A. than liquid g. In the osmotic systems:

$$\underset{\longrightarrow W}{g \mid M(W) \mid e} \qquad \underset{\longleftarrow W}{g \mid M(W) \mid q} \qquad \underset{\longrightarrow W}{g \mid M(W) \mid d} \quad . \tag{4}$$

the water diffuses, therefore, in the direction of the arrows.

Corresponding properties obtain for the isentonic W-curves as for the isotonic W-curves; then, however, we have to substitute point W by an other point, which we shall call H. We have among other things:

two isentonic curves cannot intersect or touch one another;

the O.W.n.A. of the liquids of an isotonic W-curve is greater (smaller) the further (closer) this curve is situated from (to) point H.

This point H can coincide with point W; it also may be situated, however, somewhere on one of the sides WX or WY or within the triangle.

We shall first take the simplest case viz. point H coincides with point W.

Then it appears from fig. 1 that the liquids of curve $p_2 s_2$ have a greater O.W.n.A. than those of p s and that their O.W.n.A. is greater again than that of the liquids of curve $p_1 s_1$.

Now we take a liquid e on curve $p_2 s_2$, a liquid q on $p s$ and a liquid d on $p_1 s_1$. Then we see that in the first and last of the systems :

$$\underset{\longrightarrow W}{g \mid M(n) \mid e} \qquad \underset{\text{———} \; W}{g \mid M(n) \mid q} \qquad \underset{\longleftarrow W}{g \mid M(n) \mid d} \quad . \quad (5)$$

the water must diffuse in the direction of the arrows. In the second system, however, no water diffuses ; this has been indicated by substituting the arrow by a dash.

We now take the osmotic systems :

$$g \mid M(W) \mid L \qquad g \mid M(n) \mid L \quad . \; . \; . \; . \; . \quad (6)$$

which only differ in their membranes ; the first namely has a membrane M (W) and the second a membrane M (n). With respect to the diffusion of the water we now can distinguish four cases, namely :

A. no water diffuses through the membrane M (W) but does diffuse through M (n) ;

B. no water diffuses through the membrane M (n) but does diffuse through M (W) ;

C. the water diffuses through M (n) in the same direction as through M (W) ; consequently it diffuses congruently.

D. the water diffuses through M (n) in opposite direction as through M (W) ; consequently it diffuses incongruently.

We are able to deduce these four cases from fig. 1, from which it appears at the same time that it depends on the composition of the liquid which of these cases will occur.

A. First we take the osmotic equilibria :

$$\underset{\text{———} \; W}{g \mid M(W) \mid h} \qquad \underset{\longleftarrow W}{g \mid M(n) \mid h} \quad . \; . \; . \; . \; . \; . \quad (7)$$

in which on the left side of the membrane the liquid g and on the right side the liquid h (fig. 1). As g and h are situated on the same isotonic W-curve, no W passes through the membrane in the first system. As g and h are situated on different isentonic W-curves, water does go through the membrane in the second system. If we imagine an isentonic W-curve, drawn through h, we see that this is situated closer to point W than curve $p g s$; consequently liquid g has a greater O.W.n.A. than liquid h, so that the water diffuses from h towards g, consequently in the direction of the arrow in (7).

In a corresponding way we find that the dash and the arrow in the systems :

$$\underset{\text{———} \; W}{g \mid M(W) \mid f} \qquad \underset{\longrightarrow W}{g \mid M(n) \mid f} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

indicate the direction in which W diffuses.

It is clear that we can substitute the liquid h in (7) by every other liquid of the part $g\,b$ and the liquid f in (8) by every other liquid of the part $g\,a$ of curve $a\,g\,b$. If we represent a liquid of the part $g\,b$ by $L\,(g\,b)$ and a liquid of part $g\,a$ by $L\,(g\,a)$, then, therefore, we have the systems

$$\begin{array}{ll} g \mid M(W) \mid L(gb) & g \mid M(n) \mid L(gb) \\ \overline{\qquad\qquad}\, W & \xleftarrow{\qquad\qquad} W \end{array} \quad \ldots \quad (7^a)$$

$$\begin{array}{ll} g \mid M(W) \mid L(ga) & g \mid M(n) \mid L(ga) \\ \overline{\qquad\qquad}\, W & \xrightarrow{\qquad\qquad} W \end{array} \quad \ldots \quad (8^a)$$

This shows :

if the right-side liquid is situated on the isotonic W-curve, no W diffuses through a membrane $M\,(W)$ but it does diffuse through $M\,(n)$;

through this the water diffuses towards the left when L is situated on the part $g\,b$ and towards the right when L is situated on the part $g\,a$ of the curve.

B. We now take the osmotic equilibria :

$$\begin{array}{ll} g \mid M(W) \mid L(gs) & g \mid M(n) \mid L(gs) \\ \xrightarrow{\qquad\qquad} W & \overline{\qquad\qquad}\, W \end{array} \quad \ldots \quad (9)$$

$$\begin{array}{ll} g \mid M(W) \mid L(gp) & g \mid M(n) \mid L(gp) \\ \xleftarrow{\qquad\qquad} W & \overline{\qquad\qquad}\, W \end{array} \quad \ldots \quad (10)$$

On the right side of the membrane we have in (9) a liquid of the part $g\,s$ and in (10) a liquid of the part $g\,p$ of the isentonic W-curve $p\,g\,s$.

If we take for $L\,(g\,s)$ e.g. the liquid r and for $L\,(g\,p)$ the liquid q and if we imagine the isotonic W-curves running through r and q, we see that r has a greater- and q a smaller O.W.A. than liquid g. So the arrows indicate the direction in which the water passes through the membrane.

Consequently it appears from (9) and (10) :

when the right-side liquid is situated on the isentonic W-curve, no W diffuses through the membrane $M\,(n)$, but it does diffuse through $M\,(W)$;

through this the water diffuses towards the right, when L is situated on the part $g\,s$ and towards the left when L is situated on the part $g\,p$ of the curve.

C. The curves $a\,g\,b$ and $p\,g\,s$, running through point g, divide the triangle into the four fields I, II, III, and IV. Now we first take the systems :

$$\begin{array}{ll} g \mid M(W) \mid L(\text{I}) & g \mid M(n) \mid L(\text{I}) \\ \xleftarrow{\qquad\qquad} W & \xleftarrow{\qquad\qquad} W \end{array} \quad \ldots \quad (11)$$

$$\begin{array}{ll} g \mid M(W) \mid L\ (\text{II}) & g \mid M(n) \mid L\ (\text{II}) \\ \xrightarrow{\qquad\qquad} W & \xrightarrow{\qquad\qquad} W \end{array} \quad \ldots \quad (12)$$

in which on the right side of the membrane in (11) a liquid of field I and in (12) a liquid of field II. If we take e.g. in field I the liquid d and in field II the liquid e and if besides we imagine the isotonic W-curves drawn through d and e, we see that the arrows in (11) and (12) indicate the direction in which the water diffuses. It appears from (11) and (12):

when the right-side liquid is situated in fields I or II, then the water diffuses through the membrane $M\ (n)$ in the same direction as through the membrane $M\ (W)$; so the water diffuses congruently.

D. If we take a liquid of field III or IV then we find:

$$\underset{\longleftarrow\!\!-\!\!-\!\!-\!\!-\, W}{g \mid M(W) \mid L\ (\mathrm{III})} \qquad \underset{-\!\!-\!\!-\!\!-\!\!\longrightarrow W}{g \mid M(n) \mid L\ (\mathrm{III})} \quad \ldots \quad (13)$$

$$\underset{-\!\!-\!\!-\!\!-\!\!\longrightarrow W}{g \mid M(W) \mid L\ (\mathrm{IV})} \qquad \underset{\longleftarrow\!\!-\!\!-\!\!-\!\!-\, W}{g \mid M(n) \mid L\ (\mathrm{IV})} \quad \ldots \quad (14)$$

From this appears:

when the right-side liquid is situated in fields III or IV, then the water diffuses through the membrane $M\ (n)$ in a direction opposite to that when diffusing through the membrane $M\ (W)$; so the water diffuses incongruently.

From the preceding follows among other things:

if we put a membrane $M\ (n)$ between the liquids g and L it will depend on the composition of the liquid L whether the water will diffuse congruently, incongruently or not at all. The water namely diffuses:

congruently when L is situated in fields I or II;

incongruently when L is situated in fields III or IV;

and does not pass through the membrane when L is situated on curve pgs.

The form of the isentonic W-curve does not only depend on the nature of the liquids, but also on the nature of the membrane $M\ (n)$; if we change this, the form of the curve will change also. We now assume that fig. 1 obtains for a definite membrane, which we shall call $M_1(n)$. We now imagine a liquid u (not indicated in fig. 1) on part pg of curve pgs: in the system:

$$\underset{-\!\!-\!\!-\!\!-\!\!-\, W}{g \mid M_1\,(n) \mid u} \quad \ldots\ldots\ldots \quad (15)$$

then no water will diffuse.

If we take an other membrane, however, so that curve pgs changes its form, then u is no longer situated on pg, but in fields I or III. We now imagine that u is situated in field I with a membrane $M_2(n)$ and with a membrane $M_3(n)$ in field III. In the systems:

$$\underset{\longleftarrow\!\!-\!\!-\!\!-\, W}{g \mid M_2\,(n) \mid u} \qquad \underset{-\!\!-\!\!-\!\!\longrightarrow W}{g \mid M_3(n) \mid u} \quad \ldots\ldots \quad (16)$$

the water will diffuse indeed viz. in the first system towards the left and in the second system towards the right. So it appears from (15) and (16):

when we have two definite liquids it may depend on the nature of the membrane whether water will diffuse or not and in which direction this will pass through the membrane.

In fig. 1 it has been assumed that point H coincides with point W; it may, however, be situated also on one of the sides WX or WY or within the triangle: in fig. 2 it is situated on the side WX. In fig. 1 the one terminating point of an isentonic W-curve is situated on WY and the other on WX; in fig. 2, however, there are also isentonic W-curves, the two terminating points of which are situated on WX; e.g. curve $p_1 s_1$.

As the O.W.n.A. of the liquids of an isentonic curve is greater (smaller) according as these curves are situated further from (closer to) point H, the liquids of curve $p_4 s_4$ have a greater O.W.n.A. than those of curve $p_3 s_3$; etc. So the liquid H has the smallest O.W.n.A. of all liquids. From this follows that in the system

$$\underset{\xrightarrow{\hspace{3em}} W}{H \mid M(n) \mid L} \quad \ldots \ldots \ldots \quad (17)$$

the water always diffuses towards the right, independent of the composition of the liquid L.

As curve $W\,q\,r\,s_2$ passes through point W, all liquids of this curve, therefore, have the same O.W.n.A. as the water; in the systems:

$$\underset{\overline{\hspace{3em}}\; W}{water \mid M(n) \mid q} \qquad \underset{\overline{\hspace{3em}}\; W}{water \mid M(n) \mid r} \quad \ldots \quad (18)$$

no water will pass through the membrane, notwithstanding pure water is on one side of the membrane and a solution on the other side. Of course this is not possible with a membrane $M(W)$; through this the water will always diffuse towards the right in the systems (18).

Curve $W\,q\,r\,s_2$ divides the triangle into the two fields C and In. The liquids of field C have a greater-, those of field In a smaller O.W.n.A. than the water. In the first of the systems:

$$\underset{\xrightarrow{\hspace{3em}} W}{water \mid M(n) \mid L(C)} \qquad \underset{\xleftarrow{\hspace{3em}} W}{water \mid M(n) \mid L(In)} \quad \ldots \quad (19)$$

the water, therefore, will diffuse towards the right and in the second towards the left. As the water diffuses towards the right in both systems through a membrane $M(W)$, it will, therefore, in the first system pass congruently and in the second incongruently through the membrane $M(n)$.

For the osmotic system

$$water \mid L \quad \ldots \ldots \ldots \quad (20)$$

in which L represents an aqueous solution, we may distinguish, therefore, the following cases:

1. The water diffuses through a membrane $M(W)$ towards the right (consequently towards the solution).

2. The water diffuses through a membrane $M(n)$

a. towards the right (consequently towards the solution) when L is situated within field C;

b. towards the left (consequently away from the solution) when L is situated within field In.

c. when L is situated on the line dividing the two fields, consequently on curve $W\, q\, r\, s_2$ no water will pass through the membrane.

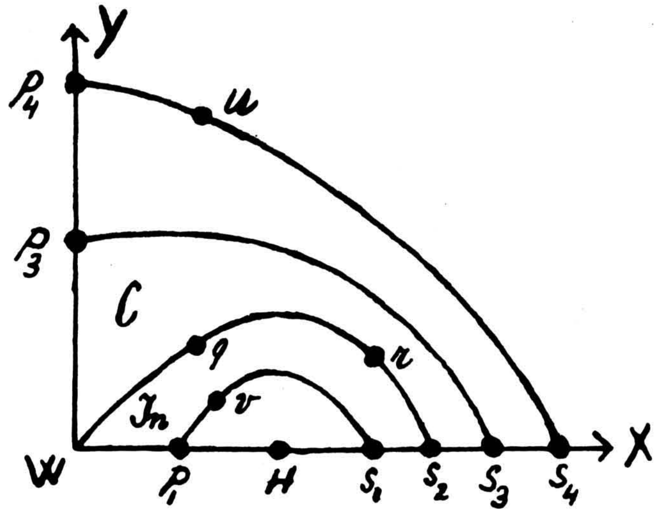

Fig. 2.

It also follows from Gen. VI that those cases are admissible. There we have deduced namely that α, β and γ in system (1) (Gen. VI) have to satisfy:

$$(\xi_x - \xi'_x)\,\alpha + (\xi_y - \xi'_y)\,\beta + (\xi_w - \xi'_w)\,\gamma > 0 \quad . \quad . \quad . \quad . \quad (21)$$

In a corresponding way we find that α, β and γ in the system:

$$\begin{array}{c} n \times water \mid n' \times L' \\ \longleftarrow \alpha X \longleftarrow \beta Y \longleftarrow \gamma W \end{array} \quad . \quad . \quad . \quad . \quad (22)$$

have to satisfy:

$$(A - RT \log \alpha)\,\alpha + (B - RT \log \beta)\,\beta + C\gamma > 0$$

in which A, B and C have finite values. We now write this in the form:

$$A'\alpha + B'\beta + C\gamma > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

When A is positive, then as $\log \alpha$ is negative, A' is positive; when A is negative, then A' will yet be positive for sufficiently small values of α: the same obtains for B'. Consequently there are always values of α and β for which A' and B' are positive, so that in (23) γ may be positive as well as negative. In agreement with the above it follows from this that in (22) the water can diffuse as well towards the right as to the left.

As a special case of the second system (19) we may take for L (In) also e.g. the binary p_1 or s_1 ; then we have the systems :

$$\underset{\xleftarrow{\qquad} W}{water \mid M(n) \mid p_1} \qquad \underset{\xleftarrow{\qquad} W}{water \mid M(n) \mid s_1} \quad . \; . \; . \quad (24)$$

in which the water diffuses from the solution towards the pure water. An example of a similar water-diffusion is found e.g. in the system :

$$\underset{\xleftarrow{\qquad} W}{water \mid M(n) \mid L \; (water + tartaric\ acid)} \quad . \; . \; . \quad (25)$$

in which on the right side of the membrane is a solution of tartaric acid of known concentration. We shall refer to this system later on.

In Gen. VI we have deduced :

if we add water to a liquid, then its O.W.A. becomes smaller.

For the O.W.n.A. of a liquid obtains, however :

if we add water to a liquid then its O.W.n.A. may decrease as well as increase.

If we take e.g. the liquid u on curve p_4s_4 (fig. 2) then the new liquid u', formed by adding a little water, will be situated on a isentonic W-curve, which is situated closer to point H than curve p_4s_4 ; therefore, the liquid u' has a smaller O.W.n.A. than liquid u.

If we take, however, the liquid v, then the new liquid v' is situated on an isentonic W-curve, which is situated further from point H than curve p_1s_1 ; so the new liquid v' has a greater O.W.n.A. than liquid v.

In the osmotic system :

$$L \mid L \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (26)$$

in which the same liquid is found on both sides of the membrane, no water passes either through a membrane M (W) or through a membrane M (n). If, however, we add a little water to one of the liquids, e.g. to the left, we get a system :

$$L' \mid L \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (27)$$

in which water does diffuse. With the aid of the above we now find :

if in system (26) we add a little water on the left side of the membrane, then water diffuses towards the right or towards the left, when there is a membrane M (n).

If we take e.g. the liquids u and v (fig. 2) then in the systems :

$$u \mid M(n) \mid u \qquad v \mid M(n) \mid v \quad . \; . \; . \; . \; . \; . \quad (28)$$

no water passes through the membrane. If, however, we add a little water on the left side of the membrane, then in the first of the systems :

$$\underset{\xrightarrow{\qquad} W}{u' \mid M(n) \mid u} \qquad \underset{\xleftarrow{\qquad} W}{v' \mid M(n) \mid v} \quad . \; . \; . \; . \; . \; . \quad (29)$$

water diffuses towards the right and in the second towards the left.

In our deductions we have assumed that point H either coincides with W or is situated on the side WX; the consideration of the other cases is left to the reader.

Besides we have discussed above only the isentonic W-curves; the same obtains, however, for the isentonic X- and Y-curves. Of course the point H of those curves is an other than that of the isentonic W-curves: that of the isentonic X-curve is situated either in point X or on one of the two sides which come together in point X or within the triangle.

(To be continued.)

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