Chemistry. — *Membrane and Osmosis.* II. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 26, 1929).

Ternary liquids and a membrane $M(W)$.

If we bring a membrane $M(W)$ into a liquid L, we can represent its composition by:

$$1 \; gr. \; Q + w \; mol \; W \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In the preceding communication [1]) we have taken a binary liquid for L; now we shall take a ternary liquid for L. When this liquid contains the substances $X + Y + W$ we may represent its composition in the usual way by a point of the triangle WXY; in the figs 1 and 2 this triangle has been drawn perspectively and in an other position than usual.

We now represent the W-amount, a liquid z gives to a membrane, by the point z' viz. by the length of the line zz' perpendicular to the plane of the triangle WXY.

When this liquid z gets all possible compositions, so that point z travels over the entire triangle, then point z' travels over a plane, which we shall call the W-plane of the membrane. This W-plane is bounded:

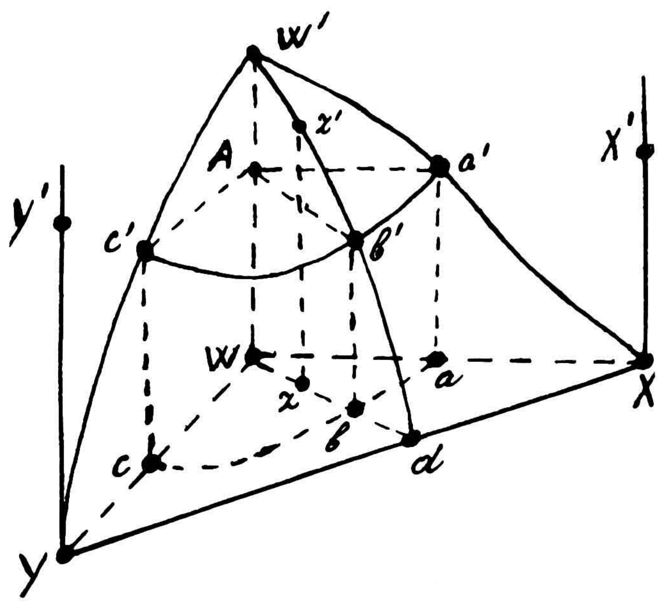

Fig. 1.

1) These Proceedings 32, 837, (1929).

in the plane $W'WXX'$ by a curve $W'a'X$; this is the W-curve of the membrane for the liquids, consisting of $W + X$.

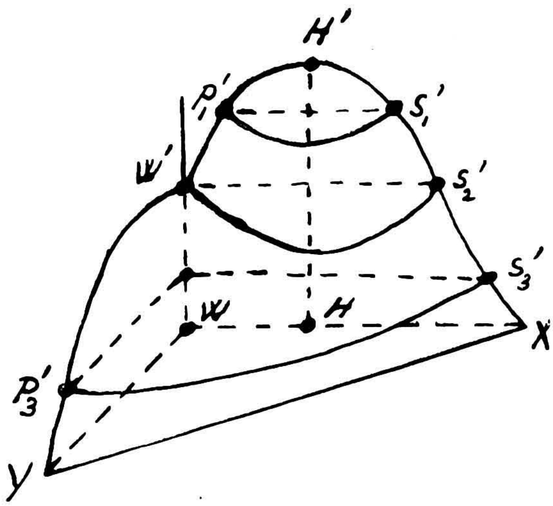

Fig. 2.

in the plane $W'WYY'$ by a curve $W'c'Y$; this is the W-curve of the membrane for the liquids, consisting of $W + Y$.

in the horizontal plane by the side XY of the triangle WXY.

The vertical plane $W'Wd$ (fig. 1) intersects the W-plane along a curve $W'z'b'd$; the points of this curve represent the W-amount, the membrane gets in the liquids of the line $Wzbd$.

In Comm. M. O. I we have deduced what has been stated in B with the aid of A_1 and A_2, namely:

the W-curve of a membrane $M(W)$ is monotonous.

In a corresponding way we can deduce now that the intersection $W'z'b'd$ is monotonous; so we find:

A_1. every flat plane, going through the axis $W'W$, intersects the W-plane of a membrane $M(W)$ according to a monotonous curve.

We shall express this more simply by:

A_2. the W-plane of a membrane $M(W)$ is monotonous.

Ternary liquids and a membrane $M(X)$ or $M(Y)$.

All that has been said above of a membrane $M(W)$ obtains of course also for any other membrane, absorbing one single substance only. If we have a membrane $M(X)$, we may represent its composition by:

$$1 \text{ gr. } Q + x \text{ mol } X \quad \ldots\ldots\ldots \quad (2)$$

if we have a membrane $M(Y)$ we may represent its composition by:

$$1 \text{ gr. } Q + y \text{ mol } Y \quad \ldots\ldots\ldots \quad (3)$$

We now imagine the X-amount of a membrane $M(X)$ represented in fig. 1 in a way corresponding to that of the W-amount of the membrane $M(W)$; we then get a plane, we shall call the X-plane of the membrane $M(X)$.

This X-plane has of course an other position than the W-plane; in fig. 1 namely it goes through the line WY and through a point X', which represents the X-amount, the membrane gets in the pure liquid X.

If we imagine the Y-amount of a membrane $M(Y)$ represented in a similar way, we get the Y-plane of the membrane $M(Y)$; in fig. 1 this plane goes through the line WX and a point Y'.

In a similar way as has been indicated above we now find:

B. the X-plane of a membrane $M(X)$ and the Y-plane of a membrane $M(Y)$ are monotonous.

Ternary liquids and a membrane $M(n)$.

If we bring a membrane $M(n)$ into a ternary liquid, consisting of the substances $W+X+Y$, we can represent the composition of this membrane by:

$$1\ gr.\ Q + w\ mol\ W + x\ mol\ X + y\ mol\ Y \quad . \quad . \quad . \quad (4)$$

We now imagine the W-, the X- and the Y-amount, a liquid z gives to this membrane, represented in fig. 1 by the points z', z'' and z''' (the points z'' and z''', which must of course be situated somewhere on line $z\,z'$, have not been indicated in fig. 1).

When this liquid z travels over the triangle WXY, each point describes a plane viz. the W-, the X- and the Y-plane of this membrane $M(n)$.

Consequently the membrane $M(n)$ has a W-, an X- and an Y-plane, while a membrane $M(W)$ has only a W-plane in these liquids, a membrane $M(X)$ only an X-plane and a membrane $M(Y)$ only an Y-plane.

Above we have seen that the W-plane of a membrane $M(W)$, the X-plane of a membrane $M(X)$ and the Y-plane of a membrane $M(Y)$ are monotonous. As we shall see later on, however, this does not always obtain any more for the W-, the X- and the Y-plane of a membrane $M(n)$.

We shall now begin by considering the W-plane; this has two boundary curves; the one is situated in plane $WW'X$ and is the W-curve of the membrane $M(n)$ for the liquids, consisting of $W+X$; the other is situated in plane $W'WY$ and is the W-curve of the membrane $M(n)$ for the liquids, consisting of $W+Y$. We may now distinguish the following cases:

C_1. both boundary curves are monotonous (fig. 1).

C_2. one of the boundary curves is monotonous, the other has a maximum (fig. 2).

C_3. both curves have a maximum.

C_4. in one or in both boundary curves occurs not only a maximum, but also a minimum.

If we have a membrane, for which C_1 obtains, we may imagine the W-plane represented by fig. 1; here not only the two boundary curves are monotonous, but also all sections with a plane, going through the axis WW'. In pure water the membrane now gets a greater W-amount than in all other binary and ternary liquids.

If we have a membrane for which C_2 obtains, the W-plane may be shaped as has been drawn in fig. 2; the boundary curve $W'Y$ is monotonous, the boundary curve $W'X$ has a maximum in H'.

We now imagine in fig. 2 also an intersection-plane $W'W\,d$ like the one in fig. 1. If we turn this from the position $W'W\,X$ into the position $W'W\,Y$, we shall first get a series of intersections with a maximum and afterwards a series of monotonous intersections; in a certain position of the plane $W'W\,d$ this maximum is situated in the point W'.

In turning the plane $W'W\,d$ we, therefore, get a series of maxima; one of these maxima is highest; this to be sure is the highest point of the W-plane; we may now distinguish two cases:

a. In fig. 2 we have assumed that the maximum H' of the boundary curve $W'X$ is also the highest point of the W-plane. We then have:

in the binary liquid H the membrane gets a greater W-amount than in all other binary and ternary liquids and than in water.

b. It may also be imagined that the highest point of the W-plane is not situated in the boundary plane. If we imagine the horizontal projection of this point represented in fig. 2 by Q, then follows:

in the ternary liquid Q the membrane gets a greater W-amount than in all binary and ternary liquids and than in water.

So from the preceding considerations appear already among other things:

a membrane $M(n)$ gets its greatest W-amount in pure water or in one of the binary or in one of the ternary liquids;

a membrane $M(W)$, however, always gets its greatest W-amount in the water.

The reader will now have no difficulty in deducing what shapes the W-plane of a membrane can have, for which C_3 or C_4 obtains.

All that has been said above of the W-plane, also obtains for the X- and the Y-plane of a membrane $M(n)$. As, therefore, each of the three planes can already have many shapes of its own, their combination will give rise to a great many cases; we shall discuss some of these cases later on.

The iso M-curves.

As we shall see immediately an infinite number of liquids exist, which will give an equal W- or an equal X- or an equal Y-amount to a membrane;

these liquids are situated on a curve which we shall call an "iso M-curve".

When these liquids give an equal W-amount to a membrane $M(W)$, we shall call this curve an "iso $W.M(W)$-curve"; if they give an equal W-amount to a membrane $M(n)$, we shall call this curve an "iso $W.M(n)$-curve".

When these liquids give an equal X-amount (or Y-amount) to a membrane $M(n)$, we shall represent these curves in a similar way. Consequently we have in all 6 kinds of iso M-curves, namely:

iso $W.M(W)$-, iso $X.M(X)$-, iso $Y.M(Y)$-curves
iso $W.M(n)$-, iso $X.M(n)$-, iso $Y.M(n)$-curves.

We shall see later on that the first three curves play quite an other part during the osmosis than the others.

The iso $W.M(W)$-, the iso $X.M(X)$- and the iso $Y.M(Y)$-curves.

As the W-plane of a membrane $M(W)$ is monotonous, we may imagine this to be represented by fig. 1. If here we suppose: $aa' = bb' = cc'$ so that the plane $Aa'b'c'$ will be horizontal, the liquids a, b and c and also all other liquids of curve abc will give the same W-amount to the membrane $M(W)$. From this appears:

curve abc is an iso $W.M(W)$-curve.

This curve divides the triangle into two fields; all liquids within field $Wabc$ (fig. 1) give a greater, all liquids within field $abcYdX$ a smaller W-amount to the membrane than the liquids of curve abc.

Now we see also that an infinite number of these curves exist; if we imagine the plane $Aa'b'c'$ higher (lower), then curve abc will be situated closer to (farther from) point W. From this appears:

D. the horizontal projection of every horizontal intersection of the W-plane of a membrane $M(W)$ is an iso $W.M(W)$-curve.

If we now imagine some iso $W.M(W)$-curves drawn in the triangle WXY of fig. 1, we see among other things:

1. Two curves can never intersect or touch one another.
2. Every straight line, going through point W, intersects a curve in one point only.
3. The W-amount which the liquids of an iso $W.M(W)$-curve give to a membrane, will become larger, the nearer this curve is situated to point W.
4. These curves are straight lines in the vicinity of point W; at a greater distance they are curved and may take various shapes.

These properties quite agree with those of the isotonic W-curves. discussed before [1]; later on we shall see to be sure that iso $W.M(W)$-curves are the same as isotonic W-curves.

[1]) Versl. Kon. Akad. v. Wet. Amsterdam, **37**, 637, (1928); these Proceedings, **31**, 814, (1928).

If in fig. 1 we now imagine also the X-plane of a membrane $M(X)$ or the Y-plane of a membrane $M(Y)$, we shall find in a way corresponding to the one described above, the iso $X.M(X)$- or the iso $Y.M(Y)$-curves.

Of course similar properties obtain for these curves as for the iso $W.M(W)$-curves.

The iso $W.M(n)$-, the iso $X.M(n)$- and the iso $Y.M(n)$-curves.

If we intersect the W-plane of a membrane $M(n)$ by a horizontal plane, then the horizontal projection of this intersection represents all liquids, giving an equal W-amount to the membrane $M(n)$. Instead of D we now have :

E. the horizontal projection of every horizontal intersection of the W-plane of a membrane $M(n)$ is an iso $W.M(n)$-curve.

If we have a membrane $M(n)$ for which the W-plane has a shape as has been drawn in fig. 1, then the same obtains for the position of the iso $W.M(n)$-curve with respect to point W as for the iso $W.M(W)$-curves, discussed above. All that has been said above in 1—4 of the iso $W.M(W)$-curves, now also obtains for these iso $W.M(n)$-curves ; however, but these are not isotonic W-curves, as we shall see later on.

We now imagine a membrane $M(n)$ for which the W-plane has a shape like that in fig. 2. If we project the horizontal intersections $p'_1\, s'_1$, $W'\, s'_2$ and $p'_3\, s'_3$ on the triangle WXY, we can imagine these projections represented by the curves $p_1\, s_1$, $W\, s_2$ and $p_3\, s_3$ of fig. 2 in Comm. [1]) Gen. VIII.

This figure shows among other things :

all liquids of curve $Wqrs_2$ give the same W-amount to the membrane as the pure water ;

all liquids within the field $Wqrs_2\,HW$ give a larger W-amount to the membrane than the pure water ; of all these liquids the binary liquid H gives the largest W-amount to the membrane ;

all liquids outside field $Wqrs_2\,HW$ give a smaller W-amount to the membrane than pure water.

Now it appears from fig. 2 of this paper and fig. 2 of Comm. Gen. VIII, that with this iso $W.M(n)$-curve point H plays a part corresponding to that of point W with the preceding curves.

All that has been said above in 1—4 of the iso $W.M(W)$-curves, now also obtains for these iso $W.M(n)$-curves, provided we replace point W in 1—4 by point H ; in the vicinity of point H, however, these curves will not be straight, but parabolic.

We have seen above that there are also W-planes, of which the highest point Q' is not situated in one of the boundary planes ; the projection Q of this point Q' will then be situated within the triangle WXY. Then there

[1]) These Proceedings, **32**, 29, (1929).

are iso $W.M(n)$-curves, surrounding point Q and situated entirely within the triangle. In 1—4 point W should now be replaced by point Q; in the vicinity of this point the curves will then be elliptical.

The above shows among other things:

F_1. for all iso $W.M(W)$-curves the properties 1—4 obtain;

F_2. for the iso $W.M(n)$-curves the properties 1—4 obtain also, but point W may or may not have been replaced by a binary or ternary point (H or Q). It depends on the nature of the membrane and on the substances X and Y, wich of these three cases will occur.

Corresponding properties as for the iso $W.M(n)$-curves obtain of course for the iso $X.M(n)$- and iso $Y.M(n)$-curves.

The absorption by a membrane.

If a membrane that has not yet absorbed strange substances, is brought into a liquid, the composition of the membrane will first change rapidly and afterwards slowly; at last follows a series of very slow changes, which may go on for months and years.

Perhaps it is allowed to imagine that during the first period the liquid enters into the intermicellary spaces, pores and little channels and fills them; at the same time the micelles also begin to absorb some of the liquid that has entered into the membrane. Under the influence of the capillary powers this said liquid may have an other composition than the liquid outside the membrane.

After all intermicellary spaces have been filled, it will of course take some time more before all micelles have also been saturated; as this absorption will generally take place much more slowly than the filling of the intermicellary spaces, the second period will naturally last much longer than the first.

In the third period a part is played by the colloidal properties of the membrane, which were to be sure also active in the first and second periods. All sorts of factors, viz. the praehistory of the membrane, the influence of the absorbed substances, etc. may change the built, the structure, the density, etc. of the micelles and the dimensions of the intermicellary spaces; the membrane certainly changes its composition. As a rule these changes take place only very slowly and perhaps they do not stop until the membrane has lost its colloidal properties.

Whereas with not-colloidal substances we can speak of a system in equilibrium, we can do so no longer when the system contains a membrane. Then we might say indeed that a series of conditions exists, determined at any moment by the condition in which the membrane is found at that moment, which condition is determined again by the praehistory and the influence of the absorbed substances.

All this shows clearly that the above discussed *W*-curve, *W*-plane etc. of a membrane, do not represent states of equilibrium ; theoretically they have different shapes every moment, although they may practically remain unchanged during a shorter or a longer time. Besides it follows from the way in which these curves and planes have to be determined experimentally, that they cannot give anything but an approximate image of their shapes, which may vary in many respects from their true shapes. We shall refer to this later on, when discussing some examples.

(To be continued.)

Leiden, Lab. of Inorg. Chemistry.