Chemistry. — "*Equilibria in systems in which phases, separated by a semi-permeable membrane*" X. By Prof. F. A. H. SCHREINEMAKERS.

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Systems with several semipermeable membranes. Double-membranes.

We now take the osmotic equilibrium:

$$E = E_1 \mid E_2 \mid E_3 \quad \ldots \ldots \ldots \quad (1)$$

in which the separate systems E_1 and E_2 and also E_2 and E_3 are separated from one another by a semipermeable membrane. Of the many possible cases we now shall consider only the case, that the two semipermeable membranes allow to pass one substance only viz. the same substance W (water). We find the equations for equilibrium by expressing:

a. that the phases of the system E_1 are in equilibrium, taken for themselves; also those of E_2 and those of E_3.

b. that the O. W. A. of E_1 is equal to that of E_2 and that of E_2 equal to that of E_3; consequently the three separate systems have the same O. W. A.

Consequently we get the same equations for equilibrium, independent which of the three separate systems in (1) is situated between the two membranes. Therefore, if one of the three osmotic systems:

$$E_1 \mid E_2 \mid E_3 \qquad E_2 \mid E_1 \mid E_3 \qquad E_1 \mid E_3 \mid E_2$$

forms an osmotic equilibrium, then both the other ones do also.

In fig. 1 in which only a part of triangle WXY is drawn, the lines drawn represent isotonic curves. We now take into consideration the osmotic system.

$$L_1 \mid L_2 \mid L_3 \quad \ldots \ldots \ldots \quad (2)$$

in which L_1 L_2 and L_3 are liquids, represented by the points 1, 2 and 3. It is apparent from the situation of those points that

$$\text{O.W.A. or } L_1 < \text{O.W.A. or } L_2 < \text{O.W.A. or } L_3.$$

Consequently we may write for (2):

$$L_1 \overset{|}{\rightarrow} L_2 \overset{|}{\rightarrow} L_3 \quad \ldots \ldots \ldots \quad (3)$$

in which the arrows indicate the direction in which the substance W

water) diffuses. Consequently in fig. 1 the liquids L_1 and L_3 move in the direction of the arrows, drawn in the points 1 and 3; we shall refer later to the movement of L_2, which takes place of course along the line $2W$.

At last a definite osmotic equilibrium shall be formed from system (3); then the three liquids are situated on an isotonic curve. It may be converted f.i. into one of the osmotic equilibria:

$$L_c \mid L_b \mid L_a \text{ or } L_h \mid L_g \mid L_f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and accidentally also into:

$$L_e \mid L_2 \mid L_d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that liquid L_2 at the finish of the osmose is again the same as at the beginning.

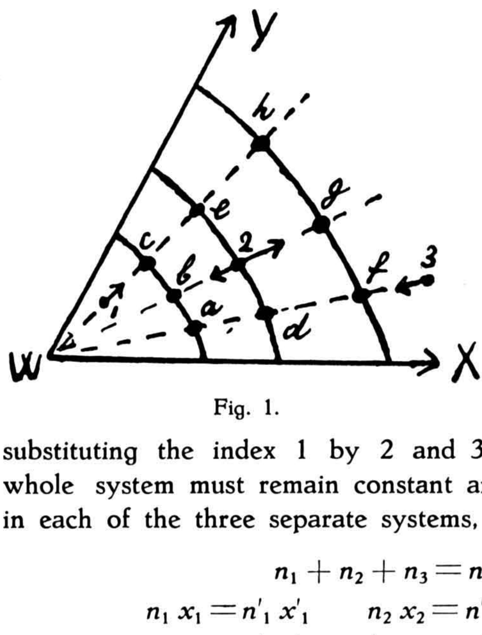

Fig. 1.

If, besides the compositions, still also the quantities n_1, n_2 and n_3 of the liquids $L_1 L_2$ and L_3 are known, then we know also the quantities n'_1 n'_2 and n'_3 and the compositions of the liquids L'_1 L'_2 and L'_3 which arise at last. We represent the composition of L_1 by $x_1 X + y_1 Y + (1 - x_1 - y_1) W$ that of L'_1 by $x'_1 X + y'_1 Y + (1 - x'_1 - y'_1) W$ those of the other liquids by substituting the index 1 by 2 and 3. As the quantity of water in the whole system must remain constant and also the quantities of X and Y in each of the three separate systems, we find the equations:

$$\left.\begin{array}{ccc} & n_1 + n_2 + n_3 = n'_1 + n'_2 + n'_3 & \\ n_1 x_1 = n'_1 x'_1 & n_2 x_2 = n'_2 x'_2 & n_3 x_3 = n'_3 x'_3 \\ n_1 y_1 = n'_1 y'_1 & n_2 y_2 = n'_2 y'_2 & n_3 y_3 = n'_3 y'_3 \end{array}\right\} \quad . \quad (6)$$

Further we still have the two equations:

$$\varphi'_1 = \varphi'_2 = \varphi'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which

$$\varphi = \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y};$$

they express that the three liquids L'_1 L'_2 and L'_3 are in osmotic equilibrium at last. We now have 9 equations for the definitions of the 9 unknowns which occur in (6) and (7); the quantities and compositions of L'_1 L'_2 and L'_3 are defined, therefore. From this appears also that the result of the osmose depends not only on the composition of the original liquids, but also on the ratio of their quantities.

The quantity of a substance W, which diffuses in a definite time by a membrane, depends not only on the difference of the O.W.A. of the two liquids, but also on the active surface of the membrane. By changing this surface, we may, therefore, regulate also the quantity of water, which diffuses in a definite time through this membrane.

Let us assume now that the system:

$$L_1 \,\vert\!\!\rightarrow L_2 \,\vert\!\!\rightarrow L_3 \text{ is converted into } E = L_c \,\vert\, L_b \,\vert\, L_a \text{ (fig. 1).}$$

As L_1 only gives water and L_3 only takes water in, those two liquids shift during the osmose always in the same direction viz. L_1 from point 1 towards c and L_2 from point 3 towards a (fig. 1). Although liquid L_2 arrives at last from point 2 in b, we yet may distinguish different cases.

a. L_2 goes without change in direction from 2 towards b.

b. L_2 goes starting from point 2 firstly in the direction towards g, returns then towards point 2 and goes further towards b.

c. L_2 goes starting from point 2 firstly towards point b, then a little further in the direction towards W and returns then towards b.

In both the latter cases we shall say that the liquid varies or swings; in case b it swings over point 2, in case c over point b.

The case, mentioned sub b, may be realised when we regulate the surface of the two membranes in such a way, that at the beginning more water diffuses from L_2 towards L_3 than L_2 takes from L_1. The case mentioned sub c can occur when the membrane between L_1 and L_2 is very large and the quantity of L_1 is large with respect to the quantity of L_2. Corresponding phenomena can occur, when system (3) is converted into one of the other equilibria (4) and (5).

If we let the liquids change places in system (2) then we get:

$$L_2 \leftarrow\!\!\vert\, L_1 \,\vert\!\!\rightarrow L_3 \qquad (8a) \qquad\qquad L_1 \,\vert\!\!\rightarrow L_3 \leftarrow\!\!\vert\, L_2 \quad . \; . \; . \quad (8b)$$

in which the arrows indicate again the direction in which the water diffuses at the beginning of the osmose. With a single example we shall show that the liquids in those systems may swing during the osmose. Let us assume that in (8a) the osmose between L_1 and L_3 takes place extremely slowly, but that between L_2 and L_1 extremely quickly. As the osmotic equilibrium between L_2 and L_1 is reached then practically almost immediately, we then get a system:

$$L'_2 \,\vert\, L'_1 \,\vert\, L'_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8c)$$

in which L'_3 differs only very little from L_3, L'_2 and L'_1 now have almost the same O.W.A., which is larger than that of L_1 but smaller than that of L_2, also smaller than that of L_3 or L'_3, therefore. Water now shall diffuse, as is indicated in:

$$L'_2 \rightarrow L'_1 \rightarrow L'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8d)$$

viz. firstly from L'_1 towards L'_3 and afterwards from L'_2 towards L'_1. The liquid L_2 in (8*a*), therefore, takes water in at the beginning of the osmose, but later it gives water again.

The equations (6) and (7) are valid not only for the conversion of system (3) but also for the systems (8*a*) and (8*b*). Consequently for the end-equilibrium it is indifferent which of the three liquids is between the two membranes; this has influence only on the way in which this equilibrium is formed.

In the osmotic system:

$$L_1 \mid L_2 \mid L_3 \mid L_4 \mid . \quad . \quad . \quad . \quad . \; L_n \; . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we have n liquids and $n—1$ membranes. We are able to show also that the osmotic equilibrium which arises at last from this, depends only on the quantities and the composition of the liquids, but that it is independent on their series. The way, in which the equilibrium sets in is dependent, however, on the series of the liquids and also on the surface of the membranes.

Let us assume that the O.W.A. of the liquids in (9) increases, according the index of the liquid being larger. We then have:

$$L_1 \rightarrow L_2 \rightarrow L_3 \rightarrow \; . \quad . \quad . \quad . \quad . \; \rightarrow L_{n-1} \rightarrow L_n \; . \quad . \quad . \quad . \quad (10)$$

in which the arrows indicate the direction in which the water diffuses. We now may imagine that L_1 and L_n during a long time change their O.W.A. only imperceptibly or not; this can take place f.i. when both liquids are present in a very large excess. This may be the case also when L_1 is f.i. water and L_n watervapour under a very low constant pressure.

While L_1 en L_n then remain unchanged, the other liquids change their composition until the same quantity of water diffuses through each membrane in the same time. As soon as this stationary state has established itself, all liquids have a definite composition and O.W.A. This stationary state depends not only on the original composition and quantities of the different liquids, but also on the surface of the different membranes.

A similar stationary state shall occur also when the liquids $L_2 \, L_3 \ldots L_{n-1}$ have the same O.W.A. at the beginning; further, of course it is indifferent whether those liquids have the same composition or not and which substances they contain.

Double-membranes.

If we compare the two osmotic systems:

$$L_1 \mid L_2 \text{ and } L_1 \mid D \mid L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

with one another, then we see that in the first one the two liquids L_1 and L_2 are in osmotic contact with one another with the aid of a single semipermeable membrane; in the second one the water, in order to diffuse from L_1 towards L_2, must pass through two semipermeable membranes, between which a phase (or system) D is found.

We now may consider the two semipermeable membranes with the included phase D as to form together a new semipermeable membrane; we call this "double-membrane with the phase D" or only "double-membrane" and we shall represent it by $\mid D \mid$ or $\mid\mid$.

We now may say that the liquids L_1 and L_2 in the second system (11) are in osmotic contact with one another with the aid of a double-membrane. Further we shall see that a double-membrane sometimes may play quite a different part as the single membrane.

We now take the osmotic system:

$$L_1 \mid Y \mid L_2 \text{ fig. 1 Comm. III} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which L_1 and L_2 are separated from one another by a double-membrane with the solid substance Y. The liquids L_1 and L_2 are represented by points within the field $WwvX$ of fig. 1 Comm. III. Further we shall see that system (12) may pass into one of the osmotic equilibria:

$$E = L'_1 \mid L \mid L'_2 \qquad (13a) \qquad E = L'_1 \mid Y + L_w \mid L'_2 \quad . \quad (13b)$$

in which all liquids are isotonic, therefore, or into the complex

$$K = L'_1 \mid Y \mid L'_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which the two liquids are not isotonic. In the latter case, therefore, the double-membrane plays the part of a wall, which is impermeable for water.

As the result of the osmose depends on the composition of the liquids L_1 and L_2 we distinguish three cases.

1. L_1 and L_2 are situated both within the field Wwm fig. 1 Comm. III. The O.W.A. of the solid substance Y is, therefore, greater than that of the liquids L_1 and L_2; at the beginning of the osmose water shall diffuse, therefore, as well from L_1 as from L_2 towards the solid substance Y. Consequently there arises a system:

$$L_1 \mid\!\rightarrow Y \leftarrow\!\mid L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It depends on the ratio of the quantities of L_1 L_2 and solid Y what shall occur further. When the quantity of solid Y is very large (in ratio to the quantities of L_1 and L_2) then equilibrium (13*b*) is formed; L'_1 and L'_2 are represented then by points of the isotonic curve *wm*.

When however the quantity of solid Y, is so small that a liquid is formed between the membranes, then an equilibrium (13*a*) arises; the three liquids are situated then anywhere within the region $W w m$ on an isotonic curve; liquid L is situated anywhere between w and W.

2. L_1 and L_2 are both situated within the field $w\ m\ X\ v$. fig. 1 Comm. III.

As the O.W.A. of the solid substance Y is smaller now than that of both the liquids, neither from L_1 nor from L_2 water can diffuse towards Y, therefore. Consequently the double-membrane prohibits the diffusion of water from L_1 towards L_2 and reversally; consequently it behaves itself now as a membrane, which checks water. Consequently the osmotic system (12) remains unchanged.

3. L_1 is situated in the field $W w m$ and L_2 in the field $w\ m\ X\ v$ of fig. 1 Comm. III.

Now water diffuses from L_1 towards the solid substance Y, so that the system $Y + L_w$ arises between both the membranes; water now diffuses from L_w towards L_2. In the beginning of the osmose is formed, therefore, the system:

$$L_1 \xrightarrow{|} Y + L_w \xrightarrow{|} L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It depends on the ratio of the quantities of L_1 L_2 and solid Y what shall occur further. We now may distinguish three cases.

a. An equilibrium (13*a*) is formed; then the three liquids are situated on an isotonic curve with the field $W w m$.

b. The equilibrium (13*b*) is formed; the three liquids are situated on the curve $w m$.

c. The osmotic complex (14) is formed; then L'_1 is situated in curve $w m$ and L_2' anywhere within the field $w m X v$. Consequently no water diffuses more from L'_1 towards L'_2, notwithstanding the O.W.A. of L'_2 is greater than that of L'_1. Consequently in the beginning the double-membrane allows water to diffuse, but it behaves itself afterwards as a membrane, which prohibits the diffusion of the water.

This case can occur when the quantity of L_1 is small with respect to the quantities of L_2 and solid Y.

Till now we have discussed only which osmotic system is formed from (12) at the end of the osmose; in similar way as in the beginning of this communication, the reader can examine for each case, which changes the liquids shall undergo viz. whether they will shift continually towards their state of equilibrium or will swing.

As is apparent from the previous, we may distinguish three cases for the osmotic action of the double-membrane.

1. The water diffuses through the double-membrane, so that an osmotic equilibrium is formed. The double-membrane behaves itself with respect to the water-diffusion as a single membrane. This is the case when both the liquids are situated within the field $W w m$ and may take place also when the liquids are situated on different sides of the curve $w m$.

Yet there is a difference between the equilibrium which is formed with the aid of a single membrane and that which is formed with the aid of a double-membrane; sometimes this difference can be very great.

When L_1 and L_2 are situated in the field $W w m$, then the result of the osmose is, that both liquids are situated also within the field Wwm; the one viz. shifts away from point W and the other towards point W, till they arrive on the same osmotic curve.

If, however, we use the double-membrane $|\,Y\,|$ with a large quantity of Y, then, as we have seen above, both liquids shift at last towards the isotonic curve $w m$. (fig. 1 Comm. III).

2. The double-membrane prohibits the diffusion of the water; it behaves itself, therefore, as a wall, which checks the water, notwithstanding the two liquids have a different O.W.A.

This is the case, when both liquids are situated in the field $w m X v$ (fig. 1 Comm. III).

3. The water diffuses firstly through the double-membrane; then the diffusion stops, although the O.W.A. of both the liquids is still different. This case may occur, when both liquids are situated on different sides of curve $w m$.

We now take the osmotic system

$$L_1 \,|\, Y \,|\, L_2 \quad \text{fig. 1 Comm. V.} \quad \ldots\ldots \quad (17)$$

in which L_1 and L_2 represent liquids of the field $W a c b$. Also here for (17) is valid, what is deduced above for system (12); of course we now have to replace the isotonic curve $w m$ and the fields $Ww m$ and $wm Xv$ of fig. 1 Comm. III by the isotonic curve $a m$ and the fields $W a m$ and $a m b c$ of fig. 1 Comm. V.

If the double-membrane contains the solid substance X, then we have the osmotic system:

$$L_1 \,|\, X \,|\, L_2 \quad \text{fig. 1 Comm. V} \quad \ldots\ldots \quad (18)$$

then the isotonic curve $b d$ and the fields $W b d a$ and $b c d$ play a corresponding part.

Hence is apparent that the solid substance, which is present in the double-membrane, may have great influence on the osmose. The double-membranes $|\,X\,|$ and $|\,Y\,|$ are viz.

both permeable for water of liquids of the field $W a m$;

both impermeable for water of liquids of the field $b\,d\,c$;
but $\mid X \mid$ is permeable and $\mid Y \mid$ is impermeable for water of liquids of the field $a\,m\,b\,d$.

When therefore, L_1 and L_2 represent, two liquids of the field $a\,m\,b\,d$, then system (17) remains unchanged, also when the two liquids are not isotonic, system (18), however, passes into an osmotic equilibrium.

If we take in the double-membrane a mixture of solid X and Y, then we have the osmotic system:

$$L_1 \,\vert\!\!\rightarrow X + Y \leftarrow\!\!\vert\, L_2 \quad \text{fig. 1 Comm. V.} \quad \ldots \quad (19)$$

in which the double-membrane is permeable for water from all liquids of the field $W\,b\,c\,a$.

As the O.W.A. of solid $X + Y$ is equal to that of liquid L_c and, therefore, greater than that of the liquids of the field $W\,b\,c\,a$, in (19) the water shall diffuse in the direction of the arrows. It now depends on the composition of the liquids L_1 and L_2 and on the ratio's of the quantities of $X\,Y\,L_1$ and L_2 which equilibrium shall be formed from (19). If we represent this by:

$$E_1 \mid D \mid E_2 \quad \ldots \quad (20)$$

then E_1 D and E_2 can be one of the equilibria:

$$X + Y + L_c \,, \quad X + L', \quad Y + L'' \text{ or } L''' \quad \ldots \quad (21)$$

Herein L' represents a liquid of the saturation-curve $b\,c$, L'' a liquid of the saturation-curve $a\,c$ and L'' an unsaturated liquid.

System (20), therefore, can represent a.o. the osmotic equilibrium:

$$L_1 \mid L \mid L_2 \quad \ldots \quad (22)$$

in which three unsatured liquids, represented by points of an isotonic curve; it can represent also the osmotic equilibrium:

$$Y + L_e \mid L \mid X + L_f \quad \text{fig. 1 Comm. V} \quad \ldots \quad (23)$$

liquid L then is situated on the isotonic surve $e\,f$. It can represent also an osmotic equilibrium:

$$X + L_g \mid L \mid X + L_g \quad \text{or} \quad L \mid X + L_g \mid X + L_g \quad \text{fig. 1 Comm. V} \quad (24)$$

in which L is a liquid of the isotonic curve, going through point g. In each of the two osmotic equilibria (24) two identical liquids L_g occur; even it is possible that an osmotic equilibrium is formed with three identical liquids, f.i.

$$X + L_g \mid X + L_g \mid X + L_g \quad \text{fig. 1 Comm. V.} \quad \ldots \quad (25)$$

This is possible only then, when the liquids L_1 and L_2 of system (19) are situated both in the field Wbc and when the complex $X+Y$ o the double-membrane is represented by a point between X and c' (imagine c' to be the point of intersection of the side XY with the line Wc, which is not drawn).

In the osmotic system

$$L_1 \mid X \mid L_2 \quad \text{fig. 1 Comm. IX.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

L_1 represents a liquid with the components $W+X+Y$ and L_2 with the components $W+X+Z$. Consequently liquid L_1 is situated in triangle WXY and L_2 in triangle WXZ of fig. 1 Comm. IX.

If L_1 is situated within the field Wdr_1 and L_2 within the field Wdr_2 then (26) passes into one of the osmotic equilibria:

$$L'_1 \mid L \mid L'_2 \ (27a) \quad L'_1 \mid X+L_d \mid L'_2 \quad . \quad . \quad . \quad . \quad (27b)$$

When in (27*a*) L is represented f. i. by point q then L'_1 is situated on qq_1 and L'_2 on qq_2. When the double-membrane contains much solid X then the equilibrium (27*b*) is formed, L'_1 is situated then on curve dr_1 and L'_2 on curve dr_2.

The osmotic system

$$L_s \mid X \mid L_w \quad \text{fig. 1 Comm. IX} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

may pass into an osmotic equilibrium (27*a*) with three unsaturated isotonic liquids; it can form also one of the systems:

$$E = L_t \mid X+L_d \mid L_v \qquad K = L_t \mid X \mid L_u \quad . \quad . \quad . \quad . \quad (29)$$

The first is an osmotic equilibrium; the latter is a complex in which L_u has a greater O.W.A. than L_t. The diffusion of water, however, is also prohibited by the double-membrane.

The reader may easily deduce the other cases, also when we use the double-membranes $\mid Y \mid$ or $\mid X+Y \mid$. I only wish to draw the attention to the fact that the double-membrane $\mid X \mid$ is impermeable for water from liquids of the fields dr_1ab and dr_2Zg, the double-membrane $\mid Y \mid$ for water from liquids of the fields acb and $ehZg$ and the double-membrane $\mid X+Y \mid$ for water from liquids of the field $fiZg$.

(*To be continued*).