Chemistry. — *On some special cases of osmosis in binary systems.* By F. A. H. Schreinemakers.

We take an osmotic system

$$L(W + X) \mid L'(W + X) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with a membrane permeable for the two substances W (water) and X. In order to concentrate our thoughts we put the liquid with the greater W-amount on the left side and consequently that with the greater X-amount on the right side of the membrane. If we represent the substances W and X by the points W and X and the liquids L and L' by the points L and L' of the line WX, then point L will consequently be situated to the left of point L' (fig. 1).

With respect to the directions in which the substances W and X flow through the membrane, we can now imagine four $D.T.$'s, namely

$$
\left.
\begin{array}{llll}
 & X & W & \\
a) & \leftarrow & \rightarrow & \\
b) & \leftarrow & \leftarrow 0 * & \\
 & X & W & \\
c) & \rightarrow 0 * & \rightarrow & \\
d) & [\rightarrow 0 * & \leftarrow 0 *\,]
\end{array}
\right\} \quad . \quad . \quad (2)
$$

in which the sign 0 indicates an incongruent- and the sign $*$ a negative direction of diffusion; in binary systems those two directions always coincide (in systems with three or more substances this is not the case).

Of these four $D.T.$'s the incongruent one (viz. d) is not possible and for this reason it has been put between parentheses; the other three are possible indeed; experimentally we have until now indeed found examples of a and b, but not yet of c.

If we now leave system (1) to itself, it will towards the end of the osmosis pass into a system:

$$L_e(W + X) \mid L_e(W + X) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the same liquid e is found on both sides of the membrane. As a special case we can imagine the quantity of this liquid e approaching zero on one of the sides of the membrane.

We imagine the final liquid e represented in fig. 1 by a point e, which must of course be situated somewhere between L and L'; the place of this point e has been determined by the ratio of the quantities of L and L' of system (1).

From this it follows that during the osmosis the points L and L' will move and will meet at last in point e. We now may assume that the two

liquids L and L' will move towards point e during the entire osmosis, namely according to the scheme:

$$\rightarrow L \qquad \leftarrow L'$$

The X-amount of liquid L then will continuously increase during the osmosis and that of liquid L' will decrease until both liquids get the same composition in point e.

Although in all systems investigated by us until now the osmosis takes place according to the scheme, discussed above, other cases also are possible for all that. It is possible namely with respect to the directions in which the liquids L and L' may move at a certain moment of the osmosis to imagine four cases, viz.:

$$
\begin{array}{llll}
 & L & L' & \qquad\qquad L \qquad L' \\
1) & \rightarrow & \leftarrow & \quad 3) \;\; \leftarrow \square \qquad \leftarrow \\
2) & \rightarrow & \rightarrow \square & \quad 4) \; [\leftarrow \square \qquad \rightarrow \square \;]
\end{array}
\right\} \quad . \quad . \quad . \quad (4)
$$

which we shall call the M.S.'s (moving schemes) of the system.

When a liquid approaches point e, we shall say that it moves normally or that it changes its composition normally; when a liquid moves away from point e, however, we shall say that it moves anormally or that its composition changes anormally [1]; the sign $\ulcorner$ placed with an arrow indicates an anormal movement or change. We now shall deduce:

the $M.S.$ N[0]. 4, placed between parentheses, in which the two substances move anormally, is not possible; the three other $M.S.$'s are possible indeed.

In order to illustrate the above, we first take a system:

$$
\left.
\begin{array}{l}
L\,(W + X)\,|\,L'\,(W + X) \\
DT\,a. \qquad \leftarrow X \qquad \rightarrow W
\end{array}
\right\} \quad . \quad . \quad . \quad . \quad (5)
$$

in which X and W flow through the membrane according to $D.T.\ a.$ As liquid L now absorbs X and gives off W, two factors consequently coöperate in order to cause the X-amount of L to increase; consequently in fig. 1 point L will move $\rightarrow$. As it appears in a similar way that point L' will move $\leftarrow$, follows the $M.S.$ N[0]. 1, namely:

$$\rightarrow L \qquad \leftarrow L' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which the two liquids move normally and consequently also change their compositions normally.

---

[1] The reader will easily see that a normal (anormal) movement of a liquid will also cause a normal (anormal) change of its X- and W-amounts.

With reference to future considerations we shall deduce this in still another way; for this reason we now represent the $D.T.$ a by:

$$\leftarrow a\,X \qquad \rightarrow \gamma\,W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which a and γ indicate the very small quantities of X and W, flowing through the membrane between the moments t and $t + dt$. We now distinguish two cases.

$$W_1 \xleftarrow{\qquad d'_1 \qquad} \bullet \underset{W \quad L}{\qquad} \bullet \underset{u}{\qquad d'_2 \qquad} \underset{L'}{\qquad d_2 \qquad} \bullet \underset{X}{} \xrightarrow{\quad d_1 \quad} X_1$$

Fig. 1

1^0. When $a > \gamma$ we may say that $a - \gamma$ quantities of a mixture have diffused towards the left. This mixture then contains a positive quantity $a : (a - \gamma)$ of the substance X and a negative quantity $-\gamma : (a - \gamma)$ of water. If we now represent the X-amount of this mixture by z, (and consequently its W-amount by $1 - z$) we have:

$$z = \frac{a}{a - \gamma} \quad \text{and} \quad 1 - z = \frac{-\gamma}{a - \gamma} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that $z > 1$. As $z > 1$, we cannot represent this diffusing mixture in fig. 1 by a point between W and X. If, however, we lengthen line WX up to a point X_1, which we imagine infinitely far away, this mixture is situated in a point d_1 somewhere between X and X_1. As this mixture is absorbed, by liquid L and given off by L', L will diffuse $\rightarrow$ and $L' \leftarrow$. In this way we find the $M.S.$ $N^0.$ 1.

2^0. When $a < \gamma$, we may say that $\gamma - a$ quantities of a mixture have diffused towards the right. This mixture then contains a negative quantity $-a : (\gamma - a)$ of the substance X and a positive quantity $\gamma : (\gamma - a)$ of water. We now have:

$$z = \frac{-a}{\gamma - a} \quad \text{and} \quad 1 - z = \frac{\gamma}{\gamma - a} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so that $z < 0$. It is clear that this mixture will be situated in fig. 1 in a point d'_1 somewhere between W_1 and W. As this mixture now is given off by liquid L and is absorbed by L', we here also find the $M.S.$ $N^0.$ 1 again.

We now take the osmotic system:

$$L\,(W + X)\,|\,L'\,(W + X) \Big) $$
$$DT\,b. \quad \leftarrow X \quad \leftarrow 0 * W \Big\} \quad . \quad . \quad . \quad . \quad (10)$$

in which X and W flow through the membrane according to the $D.T.$ b:

consequently the water diffuses incongruently and negatively. If we represent this $D.T.$ by:

$$\leftarrow aX \quad \leftarrow \gamma W. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we may say that $a + \gamma$ quantities of a mixture diffuse towards the left, this mixture then contains a positive quantity $a : (a + \gamma)$ of the substance X and also a positive quantity $\gamma : (a + \gamma)$ of water; we now have:

$$z = \frac{a}{a + \gamma} \quad \text{and} \quad 1 - z = \frac{\gamma}{a + \gamma} \quad . \quad . \quad . \quad . \quad (12)$$

As z now is always positive, but smaller than 1, the diffusing mixture will now be situated in fig. 1 somewhere between W and X.

We are able to deduce, however, that this mixture cannot have every arbitrary composition [1]), but that z must satisfy:

$$(a + \gamma)(z - u) > 0 . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which u represents a point, always situated in fig. 1 between L and L'. As during the osmosis points L and L' change their places, point u will continuously shift to an other place as well.

As $a + \gamma$ is always positive, it follows from (12): $z > u$, so that in fig. 1 the diffusing mixture must be situated somewhere between u and X. We now distinguish three cases.

1^0. The diffusing mixture is situated in a point d_2 between L' and X. As the liquid L absorbs this mixture d_2, L will move $\rightarrow$; as the liquid L' gives off this mixture, L' will move $\leftarrow$. So we once more get the $M.S.$ N^0. 1, namely:

$$\rightarrow L \quad \leftarrow L'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

2^0. The diffusing mixture is situated in a point d'_2 between u and L'. As liquid L absorbs this mixture, L will move again $\rightarrow$; as liquid L' gives off this mixture, L' now will not move $\leftarrow$ but $\rightarrow$. We then get the $M.S.$ N^0. 2, namely:

$$\rightarrow L \quad \rightarrow \square L' \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

in which the liquid L' moves anormally.

3^0. The diffusing mixture accidentally coincides with point L'. As liquid L' now gives off a mixture having the same composition as liquid L', this liquid will not change its composition and consequently point L' will not change its place either. We then have a transition $— M.S.$ between N^0. 1 and N^0. 2 which we shall represent by:

$$\rightarrow L \quad -\square L' \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

[1]) These Proceedings, **32**, 1305 (1929).

As liquid L does change its composition, this condition will last a single moment only; we shall refer to this later on.

We now take the osmotic system:

$$L\,(W+X)\ |\ L'\,(W+X)$$
$$DTc.\quad\to 0*X\quad\to W\ .\ .\ .\ .\ .\ (17)$$

in which X and W flow through the membrane according to the $D.T.\ c$; so the substance X now diffuses incongruently and negatively.

In a similar way as above we find that the diffusing mixture must be situated now somewhere between W and u, so that we may distinguish three cases again. We find namely:

1^0.   when the diffusing mixture is situated between W and L, we have the $M.S.\ N^0.\ 1$, namely:

$$\to L\quad\leftarrow L'\ .\ .\ .\ .\ .\ .\ .\ (18)$$

2^0.   when the diffusing mixture is situated between L and u, we have the $M.S.\ N^0.\ 3$, namely:

$$\leftarrow \square\, L\quad\leftarrow L'\ .\ .\ .\ .\ .\ .\ .\ (19)$$

3^0.   when accidentally the diffusing mixture coincides with point L, we have the transition $—M.S.$ between $N^0.\ 1$ and $N^0.\ 3$, namely:

$$-\square\, L\quad\leftarrow L'\ .\ .\ .\ .\ .\ .\ .\ (20)$$

which will occur only during a single moment of the osmosis.

From the preceding considerations it follows among other things:

1^0.   normal movement (change in concentration) of the two liquids will occur always when W and X flow through the membrane congruently $(D.T.\ a)$; it may occur also when one of the substances diffuses congruently and the other incongruently $(D.T.\ b$ or $c)$.

2^0.   anormal movement (change in concentration) of one of the liquids is possible only when one of the substances diffuses congruently and the other incongruently $(D.T.\ b$ or $c)$; for this, however, the diffusing mixture must besides necessarily be situated between L and L'.

3^0.   anormal movement (change in concentration) of both the liquids at the same time is not possible.

We can say also:

1^0.   the $M.S.\ N^0.\ 1$, namely

$$\to L\quad\leftarrow L'.\ .\ .\ .\ .\ .\ .\ .\ .\ (21)$$

occurs when the diffusing mixture is situated on the left side of L or on the right side of L'.

2^0. the $M.S.$ N^0. 2, namely

$$\rightarrow L \qquad \rightarrow \square\, L' \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

occurs when the diffusing mixture is situated between u and L'.

3^0. the $M.S.$ N^0. 3, namely

$$\leftarrow \square\, L \qquad \leftarrow L' \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

occurs when the diffusing mixture is situated between L and u.

We also may apply these considerations to osmotic systems, in which the composition of one of the liquids is kept constant in some way or other during the entire osmosis, so that only one of the two liquids is variable. Of the numerous cases I shall discuss only a few.

In the osmotic system (10) two $M.S.$'s may occur, as we have seen before in (14) and (15). When namely the diffusing mixture is situated in point d_2 between L' and X, then (14) obtains viz. $M.S.$ N^0. 1 ; when, however, the diffusing mixture is situated in a point d'_2 between u and L', then (15) viz. $M.S.$ N^0. 2 obtains.

If we now keep the composition of the left side liquid of system (10) constant, we get the system :

$$inv\, L\,(W + X) \mid L'\,(W + X)$$

$$D.Tb. \qquad \leftarrow X \qquad \leftarrow 0 * W \; . \; . \; . \; . \; . \; . \quad (24)$$

We now assume that the diffusing mixture is situated in a point d'_2 between u and L', so that (15) obtains. From this follows for the variable liquid L' of system (24)

$$\rightarrow \square\, L \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

So during the osmosis the variable liquid moves away from the invariant liquid L, which remains in its place of course.

If, however, we keep the composition of the right side liquid of system (10) constant, we get the system :

$$L\,(W + X) \mid inv\, L'\,(W + X)$$

$$DTb. \qquad \leftarrow X \qquad \leftarrow 0 * W \; . \; . \; . \; . \; . \; . \quad (26)$$

When both systems (24) and (26) have the same liquids L and L' and the same membrane, they also have the same $D.T.$ b and the same diffusing mixture d'_2 so that now also (15) obtains. From this now follows for the variable liquid L of system (26)

$$\rightarrow L \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (27)$$

So now the variable liquid will approach the invariant liquid, whereas in (24) it moves away from it.

It follows among other things from the preceding considerations that the variable liquid L' of an osmotic system

$$inv\, L\,(W + X) \mid L'\,(W + X) . \qquad . \quad . \quad . \quad . \quad . \quad (28)$$

may move normally or anormally, namely

$$\leftarrow L' \quad \text{or} \quad \rightarrow \square\, L' \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

It depends upon the position of the diffusing mixture which of these two cases will occur. As during the osmosis liquid L' and consequently also the diffusing mixture change continuously, we may put the question:

Can the direction, in which the variable liquid moves, turn round during the osmosis?

This is not possible, however. Let us assume namely that the variable liquid should move first in the one- and afterwards in the opposite direction, then there will be a series of points in which the variable liquid has been twice. If we call one of these points q, we should during the osmosis twice have the system:

$$inv\, L\,(W + X) \mid L'\,(q) \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

in which the variable liquid L' would move one time towards the left, and an other time towards the right. As, however, the system both times has the same liquids and the same membrane, this is not possible.

Such a turning round of the movement could consequently occur experimentally only then when the nature of the membrane should change considerably during the osmosis; we shall leave this case, which embraces a combination of all previous ones, out of consideration here.

When the diffusing mixture of system (24) viz.

$$inv\, L\,(W + X) \mid L'\,(W + X)$$
$$DTb. \quad \leftarrow X \quad \leftarrow 0 * W \quad . \quad . \quad . \quad . \quad . \quad (31)$$

is situated in a point d'_2 between u and L' (fig. 1) for the variable liquid obtains:

$$\rightarrow \square\, L' . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

We now may put the question: what composition will this liquid L' get towards the end of the osmosis?

As the movement of liquid L' can not turn about, L' will come nearer to X continuously (unless, as we shall see further on, something else happens, namely the setting in of a stationary state). If we now imagine X to be a liquid, then (31) at a certain moment would pass into a system:

$$inv\, L\,(W + X) \mid L'\,(X) \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

in which the variable liquid consists of pure X; it is clear now that the

osmosis in this system must now take place according to $D.T.$ a or c, namely:

$$a) \leftarrow X \rightarrow W \qquad c) \rightarrow 0 * X \rightarrow W \quad . \quad . \quad . \quad . \quad (34)$$
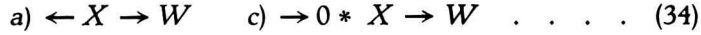
As, however, in system (31) the $D.T.$ b occurs, b must at a certain moment pass into a or c. If we compare b with a and with c, and if we bear in mind that the incongruent $D.T.$ (viz. d) cannot occur, we see that b must pass into a; we then have the transition $-D.T.$:

$$\leftarrow X \qquad - W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

so that only the substance X diffuses towards the left; consequently the diffusing mixture is now situated in point X.

From this it appears that the diffusing mixture out of point d'_2 sooner comes to point X than liquid L'; so at a certain moment of the osmosis
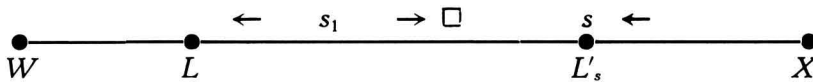
Fig. 2

the diffusing mixture will coincide with point L'. If in fig. 2 we represent this point by s, we now have an osmotic system,

$$inv\, L\,(W + X) \mid L'_s\,(W + X) \quad . \quad . \quad . \quad . \quad . \quad (36)$$
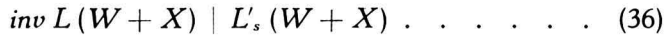
in which liquid L' gives off a diffusing mixture, now having the same composition as liquid L'. Now a stationary state sets in, which we represent by:

$$inv\, L\,(W + X) \mid stat.\ L'_s\,(W + X) \qquad - L'_s \quad . \quad . \quad (37)$$
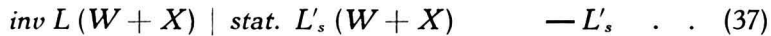
The variable liquid now does not change its composition any more, but its quantity decreases continuously until at last all the liquid on the right side of the membrane will disappear. I shall refer to this later on.

From this it appears that system (31) cannot pass into (33), but that first the stationary system (37) will be formed, in which the variable liquid will disappear at last.

Above we have seen that in a point s (fig. 2) the diffusing mixture of system (31) can get the same composition as the variable liquid; in general, however, this will take place a second time in a point s_1 between L and s (fig. 2). We then have the system:

$$inv\, L\,(W + X) \mid L'_{s_1}\,(W + X) \quad . \quad . \quad . \quad . \quad (38)$$
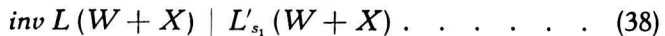
which is also stationary, but in unstable condition. If namely we imagine

that the diffusing mixture through some little disturbance or other comes a little to the left (or to the right) of point s_1, then the variable liquid L' will move $\rightarrow \square$ viz. towards s (or $\leftarrow$ viz. towards L) and arrive at last in point s (or L).

With the aid of these considerations we are now able to answer also the question: in what direction will the variable liquid of an arbitrary system:

$$inv \, L \, (W + X) \, | \, L' \, (W + X) \quad . \quad . \quad . \quad . \quad . \quad (39)$$

move during the osmosis and what composition will this liquid get towards the end of the osmosis? We now distinguish several cases.

1^0. When no stationary point occurs, the variable liquid moves normally viz. $\leftarrow$; then a system:

$$inv \, L \, (W + X) \, | \, L \, (W + X) \quad . \quad . \quad . \quad . \quad . \quad (40)$$

occurs, in which the variable liquid has the same composition as the invariant liquid.

2^0. When two stationary points s_1 and s (fig. 2) occur, we distinguish three cases.

  a. when at the beginning of the osmosis the variable liquid is situated between L and s_1 (fig. 2), then it moves $\leftarrow$ viz. normally; system (39) then passes into (40).

  b. when at the beginning of the osmosis the variable liquid is situated between s and X, it also moves $\leftarrow$ viz. normally; system (39) then passes into system (37) in which the liquid on the right side of the membrane disappears.

  c. when at the beginning of the osmosis the variable liquid is situated between s_1 and s, then it moves $\rightarrow \square$ viz. anormally; now system (39) also passes into (37), so that now the right side liquid disappears also.

In the osmotic system

$$L \, (W + X) \, | \, L' \, (W + X). \quad . \quad . \quad . \quad . \quad . \quad (41)$$

in which the two liquids are variant, the liquids may move according to one of the $M.S.$'s Nos 1, 2 or 3. We now are able to deduce that towards the end of the osmosis system (41) will pass into a system (3), in which the liquids on both sides of the membrane have the same composition, but in which the quantity of one of these liquids also can approach zero. Although a consideration of these cases is left to the reader, I yet wish to draw the attention to a single point.

Above namely we have seen that the movement of a variable liquid cannot turn round when the other liquid is invariant; this is possible, however, when both the liquids are variant and one of them e.g. L' comes

with an anormal movement in a stationary point s (fig. 2), belonging to the other liquid L. Then, however, no stationary state will set in because liquid L (which is not invariant now, but variable) then changes its composition, so that the stationary point s shifts its place also. I leave a further consideration to the reader.

Lab. of Inorg. Chemistry.

Leiden.