Chemistry. — *Osmosis of ternary liquids. General considerations* II. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 29, 1927).

The changes in concentration of the liquids; normal and anormal apparent osmosis.

If the liquids of the osmotic system

$$L \mid L' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

travel along the osmosis-path, then the concentrations of the substances X Y and W change every moment. If we only consider the concentration of each of those substances separately, without considering them in their mutual relation, then we might draw conclusions from this, which would sometimes be absolutely in variance with reality.

For it is impossible to deduce only from the change of the concentration of one of the substances, in which direction this substance diffuses through the membrane; for this we have to know the change of the concentration of *all* substances.

As, in examining the osmosis, the changes in the concentrations of liquids are most striking, we shall discuss them first; with this we shall at the same time have occasion to point at some examples of this apparent osmosis.

If we assume, to concentrate our thoughts, the liquid on the left side of the membrane has a smaller amount of X than the right side liquid, we can distinguish the following cases.

a. The amount of X of the left side liquid becomes greater and that of the right side liquid becomes smaller. We represent this by the signs:

$$\uparrow < \downarrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

The sign $<$ indicates that the left side liquid has a smaller amount of X then the right side liquid. The left side arrow $\uparrow$ which is pointed upwards indicates that the amount of X of the left side liquid increases; the right side arrow $\downarrow$ which is pointed downwards indicates that the amount of X of the right side liquid decreases.

b. The X-amount of both liquids increases; we represent it by:

$$\uparrow < \uparrow^{*} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

The meaning of it is clear now. To the meaning of the sign * near the right arrow we shall refer later on.

c. The X-amount of both liquids decreases; we represent it by:

$$^*\!\downarrow\, < \,\downarrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

d. The X-amount of the left side liquid becomes still smaller and that of the right side liquid becomes still greater; we represent it by:

$$^*\!\downarrow\, < \,\uparrow^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

In following considerations we shall discuss experimental examples of such cases.

Now we shall say:

A. the X-amount of a liquid changes *normally*.

1. if it increases, when the liquid on the other side of the membrane has a greater amount of X;

2. if it decreases, when the liquid on the other side of the membrane has a smaller amount of X;

B. the X-amount of a liquid changes *anormally*.

1. if it increases, although the liquid on the other side of the membrane has a smaller amount of X;

2. if it decreases, although the liquid on the other side of the membrane has a smaller amount of X.

Applying this to the cases, mentioned above sub *a—d*, we see that on the side where we find the asterisk, the X-amount changes anormally; on the side where this sign * is not found, the X-amount changes normally.

In case a both liquids change normally; we now shall say that the system changes normally-normally.

In case *b* the left side liquid changes normally but the right side liquid anormally; consequently the system changes: normally-anormally.

In case *c* we shall say that the system changes anormally-normally and in case *d* that the system changes anormally-anormally.

Of course the words normal and anormal should not lead us to look upon the one phenomenon a more normal than the other.

All we have discussed above as regards the X-amount of a liquid is valid of course also for its amount of Y and W.

In order to illustrate what has been discussed just now, we take the system (1). We assume that the liquid L contains only the substances W and Y and the liquid L' only W and X. Then liquid L is represented by a point 1 on the side WY and liquid L' by a point $1'$ on the side WX of fig. 1.

We assume that curve $1\ e\ 1'$ is the osmosis-path of the system; the liquids travel along this path in the direction of the arrows.

Each line, drawn through point *e*, which intersects the osmosis-path, is a conjugation line; its points of intersection represent conjugated liquids. The lines $1 . 1'$, $3 . 3'$ and $4 . 4'$ must therefore also go through point e. The dashes at the letters m, a, b and c indicate where we have to imagine those points on the path; consequently we imagine the points m', a' and b' on branch $2'.3'$ and point c' on branch $3'.4'$.

We shall begin by considering the change of the X-amount of the liquids.

In point 1 the X-amount of the liquid L is zero; as it travels along the path $1.e$ in the direction of the arrows, its X-amount increases all the time during the osmosis and it approaches that of the terminating liquid e.

In point $1'$ the X-amount of the liquid L' is represented by the length of the line $W1'$; as it travels along the path $1'.e$, its amount of X decreases all the time and it approaches also that of the terminating-liquid e.

Although all this may be read easily from fig. 1, we shall yet represent it in another diagram, by which we get a better survey also in more

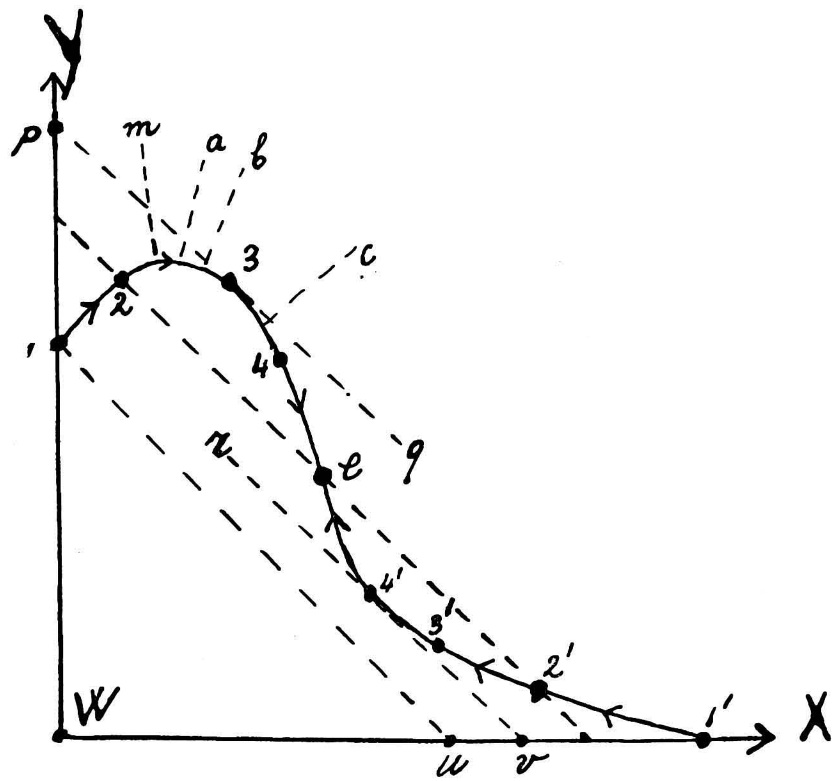

Fig. 1.

difficult cases; for this we take fig. 2 in which on the vertical axis has been drawn the X-amount and on the horizontal axis the time t of the osmosis; we shall call this the $X.t$-diagram of the system.

At the time $t=0$ viz. at the moment that the osmosis begins, L is found in point 1 of fig. 1 and so its X-amount is zero; consequently it is represented in fig. 2 by a point 1 which coincides with point 0.

After a certain time t_2 L is found in point 2 of its path; if in fig. 2 we draw on the horizontal axis this time t_2 and on the vertical axis the X-amount, then we obtain also a point 2 in this diagram.

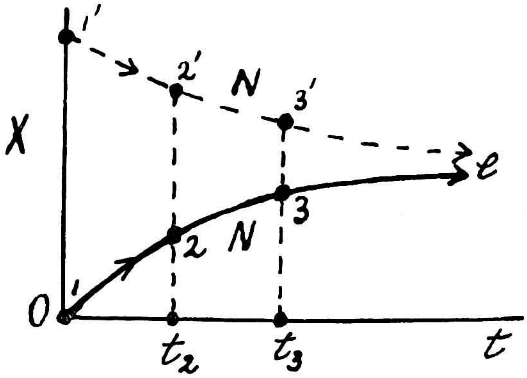

Fig. 2.

Acting in the same way with the other liquids of the path 1 . e in fig. 1 we get curve 1 . 2 . 3 . e. As the liquid L reaches the point e theoretically after an infinitely long time, point e is situated at infinite distance. We call this curve the X—L-path.

If we do the same for the liquid L' we get the curve $1'.2'.3'.e$ of fig. 2. At the moment that the osmosis begins, consequently when $t=0$, the liquid L' is found viz. in the point $1'$ of fig. 1 and its X-amount is represented, therefore, by the length of the line $W1'$. If in fig. 1 and fig. 2 we express the X-amount in the same unities of length, then $0\,1'$ must be $= W1'$; this has however been neglected in this and following sketch-figures.

We call this curve $1'.2'.3'.e$ the X—L'-path; point e of this path is situated also at infinite distance; consequently the X—L- and the X—L'-path approach one another asymptoticallv.

In order to facilitate the survey of these and subsequent figures, we shall draw the L-path and dot the L'-path.

From those paths it appears that we can represent the change of the X-amount by

$$\uparrow < \downarrow \quad \ldots\ldots\ldots \quad (2)$$

For the left side liquid has during the total osmosis a smaller X-amount than the right side liquid; it also appears from fig. 2 that the X-amount of the left side liquid increases continually and that of the right side liquid decreases. Consequently we may say that the system has a normal X—L- and X—L'-path; this is indicated in fig. 2 by the letter N. The total system changes its X-amount normally—normally.

As, according to (2), the X-amount of the left side liquid increases and that of the right side liquid decreases, we should perhaps be inclined to infer that the substance X diffuses through the membrane from right to left; we shall represent this by:

$$L \mid L' \longleftarrow X \quad \ldots\ldots\ldots \quad (3)$$

For this conclusion, however, is not the least foundation; it may be right or it may be wrong; we shall soon refer to a similar case, in which this is clearly shown.

We now take the Y-amount of the liquids. When liquid L is found in point 1 of fig. 1 then its Y-amount is represented by the length of the line $W.1$. In travelling along the path this Y-amount at first increases till point m and afterwards decreases in order to approach that of the liquid e; consequently in point m the Y-amount is a maximum.

If we draw in an $Y.t$-diagram (fig. 3) on the vertical axis the Y-amount of the liquids L and on the horizontal axis the time t of the osmosis, then we get a curve $1.2.m.3.e$ which has a maximum in the point m at the time t_m. We call this curve the Y—L-path.

If the liquid L' is found in point $1'$ of its path in fig. 1, then its Y-amount is zero. As this increases continually during the osmosis from point $1'$ till point e, we get, therefore, in fig. 3 a curve $1'.2'.m'\ 3'.e$ which has nothing particular in point m'. We call this curve the Y—L'-path.

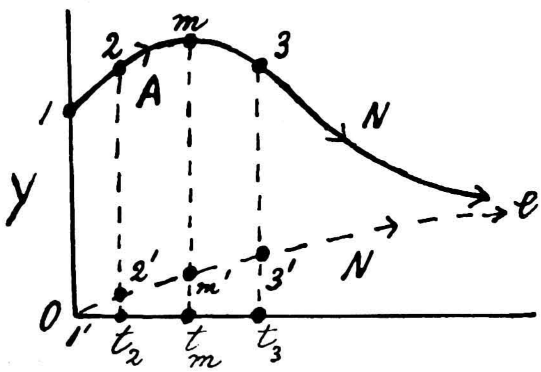

Fig. 3.

It now appears from the figure that we can represent the change of the Y-amount of both liquids, as long as they are found on the branches $1.m$ and $1'.m'$ of their paths, by

$$^{*}\uparrow > \uparrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the sign $>$ indicates that the left liquid has a greater Y-amount than the right liquid. We see from fig. 3 that the Y-amount of both liquids increases on those branches; as the Y-amount of the left liquid increases, although the right liquid has a smaller Y-amount, it changes, therefore, anormally. This is indicated in (4) by the sign $*$; in fig. 3 the letter A is written beside this branch, the letter N beside the other.

If the liquids are found on the branches $m\ e$ and $m'\ e$ of their path in fig. 3, then we can represent the change of their Y-amount by:

$$\downarrow > \uparrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore both liquids change their Y-amount normally on those branches; this is indicated in fig. 3 by the letter N. It now appears from (4) and (5):

the Y—L-path consists of an anormal branch $1.m$ and a normal branch $m.e$;

the Y—L'-path develops normally all the time.
the system changes its Y-amount.
on branch $1 . m$ (and $1' . m'$) anormally-anormally.
on branch $m . e$ (and $m' . e'$) normally-normally.

We shall represent the system which is formed by the conjugated liquids 2 and $2'$ by:

$$L_2 \mid L_2' \quad \ldots \ldots \ldots \ldots \quad (6)$$

We now may put the question: in which direction does the substance Y diffuse through the membrane?

For the change of the Y-amount of those liquids scheme (4) is valid; we see from this that the Y-amount increases on both sides of the membrane, so that it is clear that no conclusion can be made with respect to the direction in which the substance Y really diffuses through the membrane. For the change of the Y-amount is only a seeming osmosis and not only the result of the diffusicn of the substance Y alone, but also of that of the other substances. Later on we shall see that the substance Y really diffuses according to the scheme:

$$L_2 \mid L_2' \longrightarrow Y \quad \ldots \ldots \ldots \quad (7)$$

viz. from left to right.

All this is clear without further explications if we take the system:

$$L_1 \mid L_1' \quad \ldots \ldots \ldots \ldots \quad (8)$$

in which the right side liquid contains no Y. During the osmosis the substance Y must diffuse from left to right and yet the Y-amount on the left side of the membrane still increases.

In order to deduce the change of the W-amount of the two liquids we first return to the osmosis-path in fig. 1. In this we can draw a conjugation-line $2\,e\,2'$ through point e; this line runs parallel to the side $X\,Y$ of the triangle, which not has been drawn; in point 3 the tangent $p\,q$ has been drawn parallel to this side and in point $4'$ the tangent $r\,v$; also the line $1 . u$ runs parallel to this side.

The points of the line $1 . u$ represent liquids, which all have the same W-amount; the same is true for all lines, which run parallel to $X\,Y$, consequently for $r\,v$, $2 . 2'$ etc. As, however, the line $1 . u$ is situated closer to the anglepoint W than the line $r\,v$, the liquids of $1 . u$ have a greater W-amount than those of the line $r\,v$; the latter having again a greater W-amount than those of the line $2 . 2'$ etc. Hence follows:

of all liquids of the L-path (curve $1 . 2 . e$) the liquid in point 3 has the smallest W-amount; this increases from point 3 as well towards 1 as towards e; the W-amount is, therefore, a minimum in point 3;

of all liquids of the L'-path (curve $1' . 2' . e$) the liquid in point $4'$ has the greatest W-amount; this decreases from this point as well towards $1'$ as towards e; the W-amount is, therefore, a maximum in point $4'$.

There exist two conjugated liquids viz. 2 and 2′ which have the same W-amount; this is equal to that of the termination-liquid e.

Now it is easy to draw the path of the liquid L in a $W.t$-diagram; this is represented in fig. 4 by curve 1 . 2 . 3 . 4 . e which has a minimum in point 3.

The path of the liquid L' which must have a maximum in point 4′ is represented by the curve 1′. 2′. 3′. 4′. e. It appears from fig. 1 that the liquid 1 has a greater W-amount than the liquid 1′; consequently in fig. 4 point 1 must be situated over point 1′.

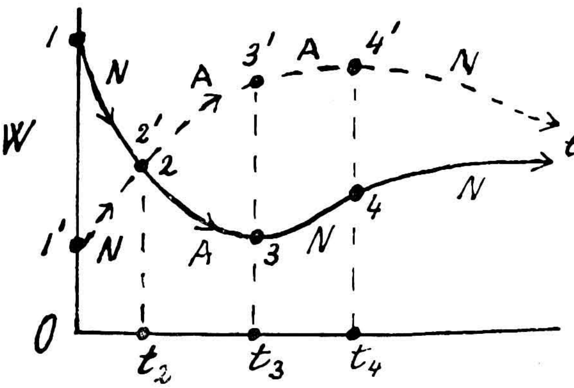

Fig. 4.

As we have seen above, the conjugated liquids 2 and 2′ have the same W-amount; consequently the L- and L'-path must intersect one another in fig. 4 in a point, which represents the W-amount of those liquids 2 and 2′. As this W-amount is equal to that of the terminating-liquid e, a horizontal line, drawn through this point of intersection must go through the point e situated at infinite distance.

We now divide the L-path into the four branches 1 . 2, 2 . 3, 3 . 4 and 4 . e and the L'-path of course into the corresponding branches 1′. 2′, 2′. 3′, 3′. 4′ and 4′. e. We now can represent the change of the W-amount of the liquids by the following scheme:

$$\begin{array}{ccccc} 1.2 & 2 & 2.3 & 3.4 & 4.e \\ \downarrow > \uparrow & {}^*\!\downarrow = \uparrow^* & {}^*\!\downarrow < \uparrow^* & \uparrow < \uparrow^* & \uparrow < \downarrow \end{array} \quad . \; . \; . \quad (9)$$

From this scheme we can learn the same things as from fig. 4. We see among other things that:

on the left side of the membrane the W-amount is greater in the beginning of the osmosis (branch 1 . 2) but afterwards smaller than on the right; in point 2 it becomes equal on both sides,

on the left side of the membrane the W-amount decreases in the beginning of the osmosis (branches 1 . 2 and 2 . 3), afterwards it increases;

on the right side of the membrane the W-amount increases in the beginning of the osmosis (branches 1 . 2, 2 . 3 and 3 . 4); afterwards it decreases.

On branch 2 . 3 the W-amount of both liquids changes anormally, for the smallest W-amount here still decreases and the greater still increases.

In point 2 both liquids have the same W-amount; as this does change, we shall call this also anormal.

On branch 3 . 4 the W-amount of the left side liquid changes normally, that of the right side liquid anormally.

Consequently we may also say:

the $W—L$-path consists of a normal part (1 . 2), an anormal part (2 .3) and afterwards again of a normal part (3 . 4 and 4 . e);

the $W—L'$-path consists of a normal part (1'. 2'), an anormal part (2'. 3' and 3'. 4') and afterwards again of a normal part (4'. e);

the W-amount of the system changes:

on branch 1 . 2 (and 1'. 2') normally—normally
" " 2 . 3 (and 2'. 3') anormally—anormally
" " 3 . 4 (and 3'. 4') normally—anormally
" " 4 . e (and 4'. e) normally—normally.

We may learn all this easily as well from fig. 4 as from scheme (9).

After the previous considerations it is evident that we can draw no conclusions from the change of the W-amount of the liquids with respect to the direction in which the substance W diffuses through the membrane. Later on we shall see in which way we can deduce this direction.

We can summarise in a single scheme all that we have discussed above and what we have deduced from the figs. 1—4. As in the following communication also the points a, b and c on the path come under discussion, we include them also in the branches given.

	X	Y	W	
1 . 2	$\uparrow < \downarrow$	$*\uparrow > \uparrow$	$\downarrow > \uparrow$	
2	"	"	$*\downarrow = \uparrow*$	
2 . m	"	"	$*\downarrow < \uparrow*$	. . . (10)
m . a . b . 3	"	$\downarrow > \uparrow$	"	
3 . c . 4	"	"	$\uparrow < \uparrow*$	
4 . e	"	"	$\uparrow < \downarrow$	

Here is indicated on which side of the membrane each substance has its greatest concentration, if this increases or decreases during the osmosis, if those changes are normal or anormal, etc.

From this we may read all that has been represented in figs. 1—4 and deduced from them, so that this scheme might be substituted for the figs. 1—4. Afterwards we shall sometimes use it.

Later on in the experimental part we shall discuss examples of the systems, mentioned above, which are being examined in collaboration with Mr. B. C. VAN BALEN WALTER.

Leiden, Lab. of Inorg. Chem. *(To be continued).*