Chemistry. — *Osmosis in systems in which also liquids with constant composition.* III. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 28, 1930).

We take an osmotic system :

$$L(a) \mid inv.\ L(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which on the right side of the membrane a liquid *i*, the composition of which is somehow kept constant during the entire osmosis ; for this reason we have formerly called this liquid "invariant".

On the left side of the membrane is a "variable" liquid, viz. a liquid, the composition (and quantity) of which changes continually during the osmosis. When, as we shall assume, the membrane is permeable for all substances, then, at the end of the osmosis this variable liquid will get the same composition as the invariant liquid *i*.

In accordance with the examples, which we are now going to discuss we shall assume that the osmotic system contains the three substances *W* (water), *X* and *Y* ; we then may represent the liquids by points of a rectangular equilateral triangle *WXY*.

Now we imagine the liquids *a* and *i* in fig. 1, in which the triangle *WXY* has not been drawn, represented by the points *a* and *i*. During the osmosis the substances now diffuse through the membrane in some direction or other and with different velocities ; the variable liquid *a* then will change its composition and proceed along a path *ai*, starting in the point *a* and ending in point *i*. In Comm. I we have called this path the "up to invariant *L* (*i*) path" in order to distinguish it from the other paths, discussed there. As here no mistake is possible, however, we shall simply call it the path of the liquid *a*.

The form of this path depends upon the composition of the liquids a and *i* and on the nature of the membrane ; it does not depend, however, upon the quantity of the variable liquid *a*.

During the time the variable liquid proceeds along its path, all sorts of phenomena may occur (e.g. normal and anormal change of concentration, positive and negative, congruent and incongruent osmosis, etc.); as we have discussed them already with reference to other cases in preceding communications, we shall not consider them here.

If we substitute the variable liquid *a* of system (1) by a liquid *b*, then we get the osmotic system :

$$L(b) \mid inv.\ L(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we represent this liquid *b* in fig. 1 by point *b*, then during the osmosis it will proceed along a path *bi*. If instead of liquid *b*, we take the liquids *c* or *d* etc., then they will proceed along the paths *ci* or *di* etc.

So there exist an infinite number of paths, all meeting and terminating in point *i*; I shall call this the "bundle" of point *i*.

Perhaps one might think that these paths meet in point *i*, in the way drawn in fig. 1, viz. that each of these paths has a different direction in point *i*, or in other words that all these paths have a different tangent in

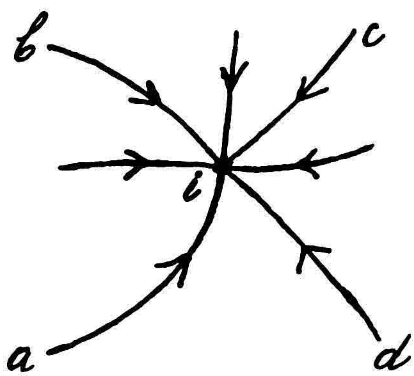

Fig. 1.

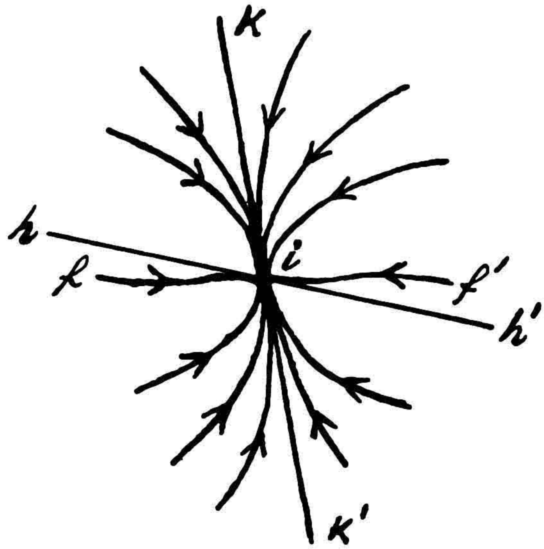

Fig. 2.

point *i*, so that in this point *i* there would be an infinite number of tangents. This is not the case, however; as we shall see in our next communication, it is possible to deduce:

all paths, meeting in an invariant point *i*, have only two tangents in this point, which we may call the axes of this bundle;

an infinite number of paths touches one of these axes (the principal axis), the other axis (secondary axis) is touched only by two paths and in special cases by one only.

If in fig. 2 we imagine the principal axis represented by *kik'* and the secondary axis by *hih'*, then all paths will touch the axis *kik'* in *i*; only the paths *fi* and *f'i* touch the axis *hih* in point *i*.

In order to elucidate the above, I shall briefly discuss some examples of bundles, which have been determined in collaboration with Mr. L. J. v. D. WOLK and Mr. H. H. SCHREINEMACHERS [1]).

[1]) For lengthier consideration, the occurring D.T.'s, the composition of the diffusing mixture, etc. comp. a dissertation, shortly to be published.

First we take an osmotic system :

$$L(z) \mid inv.\ L(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which a membrane made of a pig's bladder ; the invariant liquid *i*, which in the schematical fig. 3 we suppose represented by point *i*, contains :

$$4.680\ \%\ NaCl + 10.055\ \%\ Na_2CO_3 + 85.265\ \%\ water.$$

We now take for the variable liquid *z* first a liquid, consisting of water and NaCl only and which is represented by point *a* on the side *W*-NaCl of fig. 3 ; this liquid has the same NaCl-amount as the invariant liquid *i*.

During the osmosis the variable liquid now proceeds along path *ai*. It appears from the form of this path that the NaCl-amount of the variable liquid first increases during the osmosis, and decreases after having reached a maximum.

If we now take liquid *b* (fig. 3) for the variable liquid, it will proceed

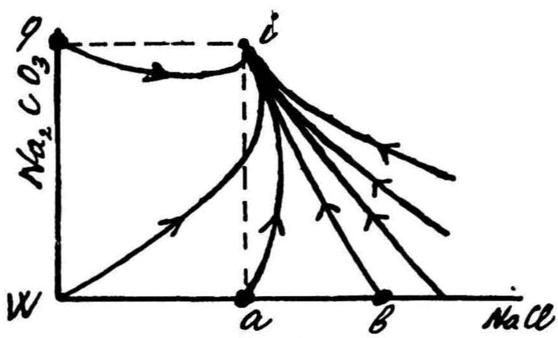

Fig. 3.

along a path *bi* ; starting from *b* this path shows at first a small curve, but farther on it is practically a straight line, touching path *ai* in *i*.

Seven paths have now been determined in this system ; it appears these determinations show that these paths, as has also been indicated in the schematical fig. 3, all touch one another in point *i*.

Path *Wi* of fig. 3 represents the special case of pure water being taken for the variable liquid *z* of system (3); we then have the system

$$water \mid inv.\ L(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which at the beginning of the osmosis the variable liquid consists of pure water. It appears from the form of this path *Wi* that the variable liquid, consisting at the beginning of the osmosis of water only, after a short time gets a certain NaCl-amount, greater than that of the invariant liquid (the path *Wi* namely intersects the dotted vertical line *Wi* ; this is necessary indeed, as otherwise path *Wi* could not touch the path *ai* and the others).

The variable liquid q consists of water and Na_2CO_3 only and has the same Na_2CO_3-amount as the invariant liquid i. It appears from the form of the path qi that the Na_2CO_3-amount of this variable liquid first decreases and afterwards increases.

If we suppose the principal axis kik' of fig. 2 drawn in fig. 3, then we see that the paths of fig. 3, as far as they have been determined, all touch part ik'; paths, touching part ik of the principal axis, have not been determined here owing to experimental difficulties. In a system, in which an invariant liquid i with the composition

$$11.724\ \%\ Na\,Cl + 6.715\ \%\ Na_2\,CO_3 + 81.561\ \%\ water.$$

however, paths have been determined, not only touching part ik', but also touching part ik of the principal axis.

We now take an osmotic system

$$L\,(z) \mid inv.\,L\,(i_1) \quad \ldots\ldots\ldots \quad (5)$$

in which the invariant liquid i_1 consists of water and NaCl only. In fig. 4, in which X represents the NaCl and Y the Na_2CO_3 it has been represented by point i_1 on side WX.

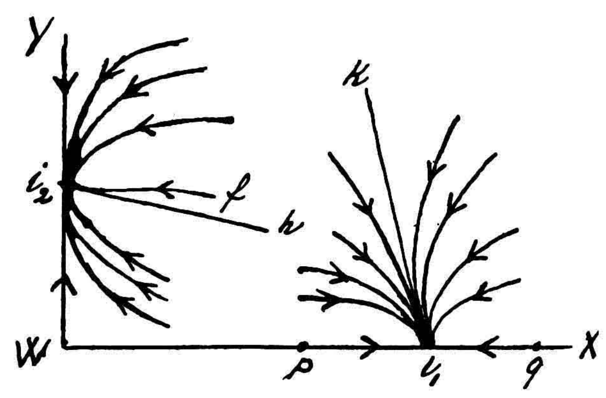

Fig. 4.

In this special case two paths are known at once; if namely we take for the variable liquid z a liquid p on side WX, then this liquid will proceed along the straight path pi_1, as p and i_1 both contain water and NaCl only. Of course the liquid q proceeds along the straight line qi_1.

Consequently two straight paths viz. pi_1 (or Wi_1) and qi_1 (or Xi_1) are situated on the side WX; so the side WX is one of the bundle of point i_1.

It appeared from the experimental determination of some paths that they all touch a line $i_1\,k$, which is, therefore, the principal axis of this bundle.

If we take an osmotic system

$$L(z) \mid inv.\, L(i_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

of which the invariant liquid i_2 consists of water and Na_2CO_3 only, we can represent it by a point i_2 on side WY of fig. 4.

It is clear now that two straight paths are situated on side WY, viz. path Wi_2 and path Yi_2 ; consequently side WY now will be one of the axes of the bundle of point i_2.

It appeared from the experimental determination of some paths that they all touch side WY ; so this side is the principal axis of the bundle. Only one single path fi_2, of course very accidentally to be determined, will now touch the secondary axis, represented by i_2h.

In the osmotic system

$$L(z) \mid inv.\, (water) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the invariant liquid consists of pure water ; so all paths of this system must meet in point W (fig. 5). [In this figure 5, X again represents the NaCl and Y the Na_2CO_3].

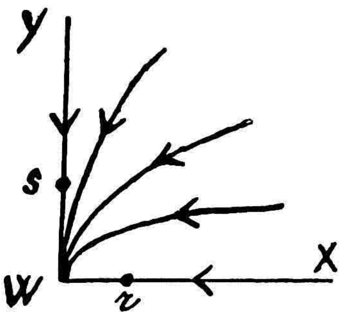

Fig. 5.

It is evident now that the sides XW and YW are straight paths ; now these sides are also the axes of the bundle of the invariant point W.

It appeared from the experimental determination of some paths that they all touch side WY ; in the vicinity of point W the paths seem to be pressed as it were against side WY ; so side WY is the principal axis and side WX the secondary axis of this bundle.

We may also extend these considerations to osmotic systems, in which a whole series of liquids and membranes are found, e.g. to the system

$$L_1 \mid L_2 \mid L_3 \mid \quad \mid \quad \mid \qquad \mid L_n \mid inv.\; L(i) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which there are n variable liquids and one invariant one. We might compare such a system in a way e.g. with a series of cells in a tissue, in which a current of blood plays the part of the invariant liquid i or with a series of vegetable cells, of wich L_n belongs to a root, growing in a soil. the composition of which might be considered invariant.

During the osmosis each of these n variable liquids now will proceed along a path ; we then get n paths, meeting in point i. The phenomena which may occur in similar systems, now may be rather complicated, because not only the nature of the n membranes, but also the ratio of their surfaces will play a great part ; I shall refer to this later on.

We might also consider an osmotic system

$$inv.\ L\,(i_1)\mid L_1 \mid L_2 \mid \quad \mid \quad \mid \qquad \mid L_n \mid inv.\ L\,(i_2) \quad . \quad . \quad . \quad (9)$$

in which n variable liquids have been surrounded by two invariant ones; at present, however, we shall only consider the simple system

$$inv.\ L\,(i_1) \overset{M_1}{\underset{\omega_1}{\mid}} L \overset{M_2}{\underset{\omega_2}{\mid}} inv.\ L\,(i_2) \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

in which is only one variable liquid. M_1 and M_2 represent the two membranes, ω_1 and ω_2 their surfaces. In accordance with an example, shortly to be discussed, we assume that this system contains the three substances W, X and Y.

When the osmosis in this system is made to begin, then W, X and Y will diffuse through both membranes in some direction or other with different velocities, so that the variable liquid changes its composition. If this system is now left alone, then, as we have seen in Communication II of this series, a stationary condition will after some time set in, which we represent by

$$inv.\ L\,(i_1) \overset{M_1}{\underset{\omega_1}{\mid}} stat.\ L \overset{M_2}{\underset{\omega_2}{\mid}} inv.\ L\,(i_2) \; . \; . \; . \; . \; . \; . \quad (11)$$

In this condition the composition of the variable liquid does not change any more; but this condition does not represent an equilibrium for all that, for the osmosis is not done and the substances W, X and Y still continue to run through the membranes. Experimentally this is proved among other things by the fact that the quantity of the stationary liquid continues to increase or to decrease all the time.

We now can deduce, as we have seen previously (l.c.) that the composition of this stationary liquid depends upon:

1. the composition of the two invariant liquids i_1 and i_2.
2. the nature of the membranes M_1 and M_2.
3. the ratio of their surfaces ω_1 and ω_2.

Every change in one of these factors will, therefore, also cause a change in the composition of the stationary liquid.

In order to elucidate the above by an example, I shall briefly discuss the system

$$inv.\ (water) \mid L\,(z) \mid inv.\ L\,(i_2) \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

which has been examined in collaboration with Mr. J. P. WERRE [1]).

1) Compare a dissertation shortly to be published.

Here the left-side invariant liquid consists of water only ; the right-side one contains :

$$4.683\ \%\ Na\,Cl + 10.096\ \%\ Na_2\,CO_3 + 85.221\ \%\ water$$

the two membranes were made of a pig's bladder. In fig. 6 in which X indicates the NaCl and Y the Na_2CO_3, these invariant liquids have been represented by W and i_2.

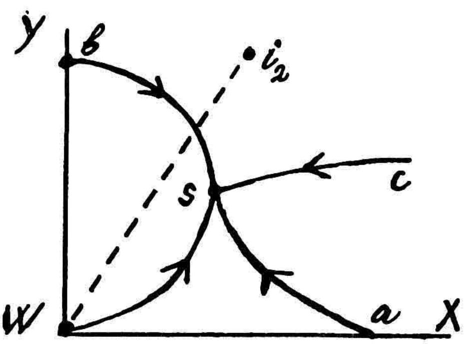

Fig. 6.

If we now take liquid a (fig. 6) for the variable liquid of system (12), then this will during the osmosis first travel along path as· as in the vicinity of this point s this liquid changed its composition only very slowly, (12) has consequently passed into the stationary system :

$$inv.\ (water)\ |\ stat.\ L\,(s)\ |\ inv.\ L\,(i_2)\ .\ .\ .\ .\ .\ \quad (13)$$

in which the liquid s has the composition :

$$3.15\ \%\ Na\,Cl + 4.74\ \%\ Na_2\,CO_3 + 92.11\ \%\ water.$$

If we take liquids b or c or W (viz. water) for the variable liquid z of system (12), then they travel respectively along the paths bs, cs or Ws (fig. 6).

In each of these cases it appeared from the continual decrease of its quantity that the osmosis still went on after the variable liquid had reached point s.

The final points s of these different paths should theoretically coincide completely ; practically, however, there were small differences. This was indeed to be expected, because the absolute establishment of the stationary condition takes place only very slowly (theoretically only after an infinite long time); besides there is a factor of more importance, namely the change in the nature (and surface) of the two membranes through several influences, active during the osmosis ; e.g. the influence of the diffusing substances, hysteresis etc.

That these influences indeed played a part here, appeared from several new determinations and also in a corresponding system, in which two membranes of cellophane (compare dissertation l.c.).

It is clear that in every stationary point s an infinite number of paths can meet ; we shall call this the bundle of the stationary point ; as we shall see in a following communication, the same rules obtain for this as for the bundle of an invariant point.

(To be continued.)

Leiden. *Lab. of Inorg. Chemistry.*