OSMOSIS OF LIQUIDS. III

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INTRODUCTION

In the preceding communications[1] we have discussed some of the phenomena presenting themselves during osmosis when the membrane either transmits a single substance or when it is permeable for all substances. Before discussing the results of other experimentally determined systems, the deduction of the direction of diffusion etc., we shall first consider from another point of view some of the phenomena, which may be met with during osmosis.

1. *The Membrane is Permeable for a Single Substance Only*

We take two liquids L and L' which both contain water and besides an arbitrary number of other substances, which may or may not be different in the two liquids. We now imagine in the osmotic system:

$$L \mid L' \qquad (1)$$

a membrane $M(W)$, *viz.* a membrane permeable for $W(W = \text{water})$. For this system we will then obtain, among other things, as we have seen in Paper I: (1) it depends upon the O.W.A. (Osmotic-Water-Attraction) of both the liquids whether water will diffuse or not; (2) when the two liquids have the same O.W.A., then no water diffuses through the membrane; (3) when the two liquids have a different O.W.A., then water will diffuse towards that side of the membrane, where the O.W.A. is greatest; (4) with this osmosis the water may go through the membrane positively or negatively and the concentrations of the substances may change normally or abnormally; with all these phenomena, as we have seen before, the nature of the membrane $M(W)$ is of importance only with respect to the velocity with which

[1] Schreinemakers, F. A. H., *J. Gen. Physiol.*, 1928, **11**, 701; 1929, **12**, 555.

the water diffuses, not, however, with respect to the direction of the diffusion; this namely is determined only by the O.W.A. (*viz.* the difference) of the two liquids.

We may also deduce this quite simply in the following way. For this purpose we imagine between the liquids L and L' an impervious wall in which are two openings; in one opening we bring a membrane A and in the other a membrane B; we imagine that both these membranes are permeable for water only. We then get a system, which we shall represent by (2).

$$L \left| \begin{matrix} A \\ \quad L' \\ B \end{matrix} \right. \tag{2}$$

Now we imagine these membranes so far apart from each other, that they can function independently of one another. If the water now did not diffuse through both membranes in the same direction, but through A in one and through B in the other direction, then a "circular current" of water would arise in (2). When the quantities of water diffusing through these membranes differ, then L and L' change their compositions, so that at last the system comes in a state of equilibrium; then the circular current will disappear. If, however, we regulate the surfaces of the membranes in such a way, that through the one as much water will diffuse towards the left as through the the other towards the right, then L and L' do not change their compositions and we get an eternal circular current. As we assume, however, that this is not possible, we may conclude that the water must diffuse through both membranes in the same direction.

If, therefore, we have a membrane permeable for water only, it will be only the O.W.A. of the two liquids which determines the diffusion-direction of the water; the nature of the membrane only influences the velocity of the diffusion.

Everything we have discussed above for the osmosis of water also obtains for any other substance S through a membrane $M(S)$, *viz.* through a membrane which is permeable only for the substance S. It then depends only upon the O.S.A. (Osmotic-S-Attraction) of the two liquids as to whether the substance S will or will not diffuse, not upon the nature of the membrane $M(S)$; this only determines the velocity of the diffusion; when both liquids have the same

O.S.A., then no S diffuses through the membrane; when the liquids have a different O.S.A., then the substance S diffuses towards that side of the membrane, where the O.S.A. is greatest; the substance S may go positively or negatively through the membrane and the concentrations of the substances may change normally or abnormally.

In Paper I we have discussed the phenomena which may occur with the osmosis through a membrane permeable for water only. All this obtains also, however, for the osmosis of the substance X through a membrane $M(X)$, *viz.* a membrane permeable for the substance X only. In these considerations the O.W.A. of the two liquids must then be substituted by their O. X. A. and the isotonic W-curves

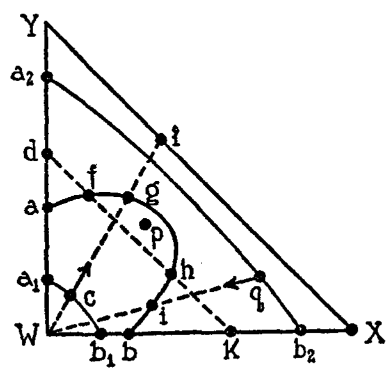

FIG. 1. This figure originally appeared as Fig. 2 in Paper I (*J. Gen. Physiol.*, 1928, **11**, 702).

by isotonic X-curves. An isotonic W-curve represents the liquids having the same O.W.A.; its two terminating points are situated on the sides WX and WY of the concentration-diagram (Fig. 1). An isotonic X-curve represents the liquids having the same O.X.A.; its two terminating points are situated, however, on the sides XW and XY of the diagram. Of course the same obtains also for the osmosis of the substance Y through a membrane $M(Y)$; then the O.W.A. of the two liquids must be substituted by their O.Y.A. and the isotonic W-curves by isotonic Y-curves, the terminating points of which are now situated on the sides YW and YX of the diagram.

2. The Membrane is Permeable for All Substances. Congruent and Incongruent Osmosis

When in a system we insert a membrane permeable for a single substance only, then the direction in which this substance will diffuse is independent of the nature of the membrane. If, however, we bring a membrane into that system, permeable for all substances, then, as we shall see further on, the nature of the membrane will indeed play a part; already in Paper II some examples have shown us that the form of the osmosis-path of a system is dependent upon the membrane; in following communications we shall discuss some more examples of it.

We are now going to ask: in which directions will the substances diffuse, when a membrane $M(n)$, *viz.* a membrane permeable for all substances, is brought into a system. In order to concentrate our thoughts, we take the osmotic system:

$$\begin{array}{ccc} & L \mid L' & \\ \text{O. X. A.} & \text{O. Y. A.} & \text{O. W. A.} \\ \longleftarrow & \longrightarrow & \longrightarrow \end{array} \qquad (3)$$

in which L and L' are two liquids of which the composition is known and containing the substances $X+Y+W$. These liquids have a definite O.X.A., O.Y.A., and O.W.A. We now assume that the left-side liquid has a greater O. X. A. than the right-side liquid; this has been indicated in (3) by the first arrow, as this points towards that side of the membrane where the O.X.A. is greatest. If we bring a membrane $M(X)$ in system (3), then the substance X will also diffuse in the direction of the first arrow, *viz.*, towards the left.

The second arrow indicates that we suppose that the O.Y.A. on the right side of the membrane is greater than on the left side; when we bring a membrane $M(Y)$ in the system, then the susbtance Y will diffuse also in the direction of the second arrow, *viz.*, towards the right.

The third arrow indicates that we suppose that the O.W.A. on the right side is greater than on the left side; consequently, through a membrane $M(W)$ the water will also diffuse towards the right. Therefore, the arrows in (3) have two meanings, of which the one follows from the other, namely: they point towards that side of the membrane, where the O.A. of a substance is greatest; they indicate the direction in which a substance diffuses through a membrane permeable for this substance only.

In system (3), therefore, the substance X will, according to our supposition, diffuse through a membrane $M(X)$ towards the left, the substance Y through a membrane $M(Y)$ and the water through a membrane $M(W)$ towards the right.

What will happen now when we bring a membrane $M(n)$ in system (3), so that all substances diffuse at the same time? Perhaps we might think that the substances must in this case also diffuse according to the arrows in (3), *viz.* from smaller towards greater O.A.; consequently X towards the left and Y and W towards the right; this is certainly possible, but not necessary; for in the case of this diffusion the nature of the membrane $M(n)$ will play a part.

If we omit the signs $>$ or $<$, and also the vertical arrows, and if we only consider the horizontal arrows, *viz.* the directions in which the substances X, Y, and W go through the membrane, then we may imagine eight cases, *viz.*:

	X	Y	W	
(1)	$\longleftarrow$	$\longleftarrow$	$\longleftarrow$	
(2)	$\longleftarrow$	$\longleftarrow$	$\longrightarrow$	
(3)	$\longleftarrow$	$\longrightarrow$	$\longleftarrow$	(4)
(4)	$\longleftarrow$	$\longrightarrow$	$\longrightarrow$	
(5)	$\longrightarrow$	$\longleftarrow$	$\longleftarrow$	
(6)	$\longrightarrow$	$\longleftarrow$	$\longrightarrow$	
(7)	$\longrightarrow$	$\longrightarrow$	$\longleftarrow$	
(8)	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	

We call each of these cases a D.T. (diffusion-type); consequently eight D.T.'s may be conceived. If, however, not only the diffusion-directions are considered, but also the velocities with which these substances diffuse, besides positive or negative and normal or abnormal osmosis, then each of the eight D.T.'s consists of an infinity of others. The relations existing between the velocities in these

D.T.'s will be left out of consideration here. In further discussions we are only going to consider the directions, so that we distinguish eight D.T.'s only.

In order to simplify a closer discussion of the subject, we shall first introduce another term; as it is we have already discussed positive and negative, normal and abnormal osmosis; now we shall distinguish in addition "congruent" and "incongruent" osmosis; that is, the substance X diffuses "congruently" through a membrane $M(n)$, when it passes through it in the same direction as through a membrane $M(X)$; consequently when X diffuses from smaller towards greater O.X.A. The substance X diffuses "incongruently" through a membrane $M(n)$, when it passes through it in the opposite direction than when going through a membrane $M(X)$; consequently when X diffuses from greater towards smaller O.X.A.

The same is also said for the substances Y and W and of course also for any other substance.

So the arrows in (3) have even a third meaning; they indicate also the congruent direction of each of the three substances. In system (3), therefore, the substance X diffuses congruently when it passes through the membrane towards the left, and the substances Y and W congruently, when they go towards the right.

If we compare the arrows of system (3) with the eight D.T.'s of (4), we see that in No. 4 the substances X, Y, and W go congruently through the membrane; for this reason we call No. 4 the "congruent D.T." of system (3).

In No. 5 each of the substances X, Y and W diffuses, however, in the opposite direction, consequently in incongruent direction; for this reason we call No. 5 the "incongruent D.T."

In the other D.T.'s *viz.*, Nos. 1–3 and Nos. 6–8, congruent as well as incongruent directions appear; we call them the "mixed D.T.'s" of system (3).

We are able to deduce thermodynamically: the incongruent D.T. is not possible; the seven other D.T.'s (*viz.* the congruent and the mixed ones) are possible, *i.e.* thermodynamically admissible; the nature of the membrane determines which of those seven admissible D.T.'s will occur.

We can prove in quite a simple manner that the incongruent D. T.

is not possible. For this reason we imagine an impermeable wall between the liquids L and L', in which there are four openings; into them we bring the membranes $M(n)$, $M(X)$, $M(Y)$ and $M(W)$. We then get a system which we shall represent by (5). We now imagine the three membranes $M(X)$, $M(Y)$, and $M(W)$ shut off at first, so that they cannot function. When the substance X diffuses incongruently through the membrane $M(n)$, *i.e.* in opposite direction as when diffusing through a membrane $M(X)$, we can open up the membrane $M(X)$ and regulate its surface in such a way that as much X runs through $M(X)$ in congruent direction as through $M(n)$ in incongruent

$$L \quad \left| \begin{array}{l} M(n) \\ \qquad L' \\ M(X) \\ M(Y) \\ M(W) \end{array} \right. \qquad (5)$$

direction; then we get a circular current of the substance X. As, however, Y and W also run through the membrane $M(n)$, the liquids L and L' will change their compositions; as the system will at last reach a state of equilibrium, this circular current of X will also disappear. When, however, Y and W both diffuse also incongruently through the membrane $M(n)$, we may also open up the membranes $M(Y)$ and $M(W)$ and regulate their surfaces in such a way that as much Y and also as much W runs in both directions. When, therefore, all substances go incongruently through the membrane $M(n)$, we can form a system in which at each moment as much X, Y, and W runs in congruent as in incongruent direction. As the compositions of the liquids L and L' do not change in this case, we should then get an eternal circular current for each of the substances. So it follows that the incongruent D.T. cannot occur.

The congruent and consequently also the incongruent direction of the substances X, Y, and W is determined by the O.X.A., the O.Y.A. and the O.W.A. of the two liquids; these O.A.'s, however, depend upon the compositions of the liquids; if we change them, the O.A.'s will also change.

The direction of the arrows in (3) is consequently determined by the composition of the liquids L and L'; for a whole series of compositions the arrows in (3) will, therefore, keep the same direction; for other compositions, however, one or more of these arrows will change their directions. If, *e.g.*, the O.Y.A. becomes greater on the left side of the membrane than on the right side, we have instead of (3):

$$\begin{array}{ccc} \text{O. X. A.} & \text{O. Y. A.} & \text{O. W. A.} \\ \longleftarrow & \longleftarrow & \longrightarrow \end{array} \qquad (6)$$

It now appears from (4) that the D.T. No. 2 is congruent and No. 7 is incongruent. When after a further change in the composition of the liquids the O.X.A. becomes smaller on the left side than on the right side, then (6) passes into:

$$\begin{array}{ccc} \text{O. X. A.} & \text{O. Y. A.} & \text{O. W. A.} \\ \longrightarrow & \longleftarrow & \longrightarrow \end{array} \qquad (7)$$

so that now D.T. No. 6 is congruent and No. 3 incongruent.

So it depends upon the composition of the liquids, which D.T. is incongruent and consequently not possible;[2] so we may say: the composition of the two liquids determines which of the eight D.T.'s is incongruent and, therefore, not possible; the nature of the membrane determines which of the seven other D.T.'s will occur.

Briefly we shall express this by saying: with the osmosis through a membrane $M(n)$ everything is possible, except all substances going incongruently through the membrane at the same time. Therefore, the nature of the membrane can have a great influence on the D.T. of a system; we shall briefly discuss some examples in which we have also been able to show this influence experimentally. We represent one of these results by:

$$\begin{array}{cccc} & X = \text{NaCl} & Y = \text{Na}_2\text{CO}_3 & W \\ \text{D. T. No. 3} & \longleftarrow & \longrightarrow & \longleftarrow \\ \text{D. T. No. 7} & \longrightarrow & \longrightarrow & \longleftarrow \end{array} \qquad (8)$$

This means the following. We took two liquids of definite compositions, containing the substances $X = \text{NaCl}$, $Y = Na_2CO_3$ and $W =$ water. We found that these substances diffused through some membranes, according to D.T. No. 3, through some other membranes,

[2] We may show that the D. T.'s No. 1 and No. 8 never can be incongruent.

however, according to the D.T. No. 7. So the diffusion-direction of the NaCl here changes with the nature of the membrane; one of the diffusion-directions of the NaCl must be congruent and the other incongruent. However, as long as we do not dispose of a membrane permeable for NaCl only, it is not possible to find out which direction is the congruent and which the incongruent.

In (8) only the horizontal arrows of the two D.T.'s have been indicated; with the aid of the complete D.T.'s we can indicate all changes, occurring at this moment of the osmosis. We found, *e.g.*, for one group of membranes:

$$\begin{array}{ccc} X & Y & W \\ *\downarrow\ <\ \uparrow* & \downarrow\ >\ \uparrow & \uparrow\ <\ \downarrow \\ \longleftarrow & \longrightarrow & \longleftarrow \end{array} \qquad (9)$$

an abnormal-abnormal-positive osmosis of the NaCl. With the second group of membranes we found:

$$\begin{array}{ccc} X & Y & W \\ *\downarrow\ <\ \uparrow* & \downarrow\ >\ \uparrow & \uparrow\ <\ \downarrow \\ \longrightarrow* & \longrightarrow & \longleftarrow \end{array} \qquad (10)$$

an abnormal-abnormal-negative osmosis of the NaCl.

This shows once more what we stated previously that from the change in concentration of a substance we cannot deduce the direction in which this has diffused through the membrane. For in (9) and (10) the X-amount on the left side of the membrane becomes smaller and on the right side it becomes greater; yet the substance X has diffused in (9) towards the left and in (10) towards the right. In the system: $X = Na_2S_2O_6$, $Y = BaS_2O_6$ and W = water, we found the D.T.'s:

$$\begin{array}{lccc} & X & Y & W \\ \text{D. T. No. 3} & \longleftarrow & \longrightarrow & \longleftarrow \\ \text{D. T. No. 4} & \longleftarrow & \longrightarrow & \longrightarrow \end{array} \qquad (11)$$

for two liquids of definite composition.

These substances, namely, diffused through a membrane of collodion according to the D.T. No. 3 and through a membrane of collodion in which was a deposit of $Cu_2Fe(CN)_6$ according to the D.T.

No. 4. So here it is the diffusion-direction of the water which changes with the nature of the membrane used; through one of these membranes, therefore, the water diffused congruently, through the other incongruently.

In the system: $X = NH_4Cl$, Y = ammonium succinate and W = water we also found for two liquids of definite composition the two D.T.'s which have been indicated in (11).

The D.T. No. 3 occurred when membranes (*a*) of collodion, (*b*) of cellophan and (*c*) of a pig's bladder were used.

The D.T. No. 4 occurred with a membrane (*d*) of collodion in which a deposit of $Cu_2Fe(CN)_6$; (*e*) of parchment and (*f*) of a pig's bladder. As is apparent from (*c*) and (*f*) the water in the system diffuses through one pig's bladder towards the left and through the other towards the right. This contrasting behaviour will have its reason in the difference in their antecedents before they were being used as membranes, such as degreasing, etc.

Now we take the osmotic system:

$$\text{water} \mid L \text{ (water + tartaric acid)} \tag{12}$$

in which on the right side of the membrane is a solution of tartaric acid of definite concentration. If we bring a membrane $M(W)$ in here, then we have the osmotic system:

$$\begin{array}{c} \text{water} \mid M(W) \mid L \\ \longrightarrow W \end{array} \tag{13}$$

in which the water, as is indicated by the arrow, will diffuse towards the right, namely towards the solution; so in this system the congruent direction of the water is towards the right.

If, however, we bring a membrane $M(n)$ in this system, then it will depend upon the nature of this membrane whether the water will diffuse towards the right or towards the left; as there is no tartaric acid on the left side of the membrane, this will of course diffuse towards the left. So we can distinguish the two D.T.'s:

$$\begin{array}{cc} \multicolumn{2}{c}{\text{water} \mid M(n) \mid L} \\ \longrightarrow W & \longleftarrow Z \\ \longleftarrow 0\,W & \longleftarrow Z \end{array} \tag{14}$$

in which the tartaric acid has been represented by Z. The sign 0 indicates that the water diffuses incongruently in the second D.T. With a membrane of cellophan we found the first D.T.; for the water diffused through this membrane towards the solution. With a membrane made of a pig's bladder we found the second D.T.; for the water diffused, just as the acid, through this membrane from the solution towards the water, consequently in incongruent direction.

It appears from the examples discussed above, that in a given system it depends upon the nature of the membrane $M(n)$ whether one or more (not all) substances will diffuse incongruently; we may also imagine membranes, through which a certain substance in a given system does not diffuse, although the membrane is permeable for this substance.

Let us take *e.g.* the system (11) in which the water diffuses through some membranes towards the left and through other membranes towards the right. As transition we may also imagine a membrane, through which no water diffuses, so that we have the transition—D.T.:

$$\longleftarrow X \qquad \longrightarrow Y \qquad —— W \tag{15}$$

Then we have a system, in which at that moment no water passes through the membrane, although the membrane is permeable for water.

A similar phenomenon often occurs during the osmosis. If we leave a system alone, so that it will run along its osmosis-path, then it often occurs that one of the substances will diffuse towards the left in one part of this path and towards the right in the other part. So during the osmosis there must be a moment, in which one D.T. passes into the other and this substance does not diffuse, of course.

These considerations may also be extended to the case that n substances pass through the membrane; then we find: (1) there are 2^n conceivable D.T.'s; (2) the composition of the two liquids determines which D.T. is incongruent and, therefore, not possible; (3) the nature of the membrane determines which of the 2^n-1 other D.T.'s will occur.

From this it appears that the composition of the two liquids and the O.A.'s of the n substances resulting from them now only play a small part; all these O.A.'s together namely determine one single D.T.

only, *viz.* the incongruent one, consequently the D.T. which is not possible. The membrane, which has the choice of the $2^n - 1$ remaining D.T.'s now plays the important part here. If, however, we put $n = 1$, *viz.* a membrane permeable for one single substance only, then the situation becomes altogether different. Then there are only $2^n = 2$ D.T.'s conceivable; the composition of the liquids determines which D.T. will be incongruent and, therefore, not possible. So now there remains only one D. T., so that the membrane has no choice any more. In accordance with the preceding we therefore find here also: in a given system a substance S will always diffuse through a membrane $M(S)$ in the same direction, *viz.* congruently; the nature of the membrane has no influence on this.

Let us imagine the case that there are six diffusing substances; then there are $2^6 = 64$ D.T.'s. If we take two liquids of definite compositions then 63 D.T.'s must still remain; it now depends upon the membrane which of those 63 D.T.'s will occur. If only we could find the membranes adapted for this, we perhaps might see these six substances diffusing in 63 different ways, and in each of these D.T.'s alternatively positive or negative and normal or abnormal osmosis may occur besides.

We must also take into consideration that the membrane is a colloidal substance, so that it may change its nature and, therefore, also its D.T., under the influence of all sorts of factors, *e.g.* the influence of the diffusing substances, age, hysteresis, etc. So we need not be surprised, when Nature, with the osmosis in vegetable and animal tissues, sometimes shows us an abundance of phenomena and a change of D.T.'s under all sorts of internal and external influences.

SUMMARY

If only one substance S passes through a membrane, the nature of this membrane is not of importance with respect to the direction of the diffusion; this is namely determined only by the O.S.A. of the two liquids.

If, however, more substances pass through a membrane, the nature of this membrane is of great importance.

If n substances diffuse through a membrane, we can distinguish 2^n cases, when we take into consideration only the direction in which

each of these substances passes through the membrane; if we call each of these cases a D.T. (diffusion-type), 2^n D.T.'s may be conceived. Now we can deduce: one of these D.T.'s is not possible, the other 2^n-1 D.T.'s are thermodynamically admissible. The composition of the two liquids determines which of the D.T.'s is not possible; the nature of the membrane determines which of the 2^n-1 other D.T.'s will occur.