OSMOSIS OF LIQUIDS. II.

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(Accepted for publication, November 22, 1928.)

INTRODUCTION.

We take an osmotic system

$$n_1 \times L_1 \mid n_1' \times L_1' \tag{1}$$

in which on the left side of the membrane are n_1 quantities of a liquid L_1 and on the right side n_1' quantities of L_1'. We now assume, in the same way as in the preceding communication,[1] that the system contains three substances, *viz.* X, Y and W (W = water); then we may represent L_1 and L_1' by the points 1 and 1′ (Fig. 3, Paper I). The position of their complex e, as we have seen previously, is determined by:

$$e1 : e1' = n_1' : n_1 \tag{2}$$

When the membrane transmits only W, during the osmosis L_1 will proceed along the line 1.4 (Fig. 3, Paper I) and L_1' along the line 1′.4′. At last the osmotic equilibrium forms:

$$n_4 \times L_4 \mid n_4' \times L_4' \tag{3}$$

Then the water diffusion has stopped; the two liquids are situated on the same isotonic W-curve ab and consequently they have the same O.W.A.

The phenomena are different, however, when the membrane transmits two or three substances. Here we shall discuss only the membrane that transmits the three substances.

[1] Schreinemakers, F. A. H., *J. Gen. Physiol.*, 1928, xi, 701.

I.

The Theoretical Osmosis Path.

We represent the liquids of system (1) by the points 1 and 1′ in Fig. 1; in order to save place, the sides and angle points of the triangle WXY have been omitted. The complex of both the liquids is represented by point e; its position has been determined by (2).

As soon as the osmosis has begun and the substances X, Y and W diffuse through the membrane in some direction or other, the liquids change their compositions. After a time t_2 the left side liquid has arrived *e.g.* in point 2 and the right side liquid in point 2′ (Fig. 1). As the quantities of the liquids have also changed now, we represent them by n_2 and n_2'. Consequently system (1) has now passed into:

$$n_2 \times L_2 \mid n_2' \times L_2' \tag{4}$$

Of course the total quantity of the two liquids remains constant during the osmosis; we have, therefore: $n_2 + n_2' = n_1 + n_1'$. The total composition of the system also remains constant; consequently the line 2.2′ also runs through point e. Instead of (2) we now have however:

$$e2 : e2' = n_2' : n_2 \tag{5}$$

After a time t_3 the left side liquid has arrived in a point 3 and the right side liquid in a point 3′; we then have a system:

$$n_3 \times L_3 \mid n_3' \times L_3' \tag{6}$$

For this we obtain:

$$n_3 + n_3' = n_2 + n_2' = n_1 + n_1'$$

The line 3.3′ also runs through point e; we now have:

$$e3 : e3' = n_3' : n_3 \tag{7}$$

Of course the same obtains for all systems that have formed during the osmosis. At the end of the osmosis the two liquids must be in osmotic equilibrium with one another. If only one substance passes through the membrane, then, as we have seen in Paper I, the two final liquids are different. If, however, the membrane is permeable with respect to all substances, then the same final liquid must form on both sides of the membrane;[2] it is clear that this liquid is represented by point e. At the end of the osmosis, therefore, we get the system:

$$L_e \mid L_e \tag{8}$$

During the osmosis the left side liquid, therefore, proceeds along a curve $1.2.3.\dots.e$, the right side liquid along a curve $1'.2'.3'.\dots.e$; the arrows indicate the direction in which theliquids proceed along these curves. We call these curves "the osmosis path" of the left and right side liquids; together they form the "osmosis path" of the system. In Figs. 2 and 4 osmosis paths have been drawn, which have

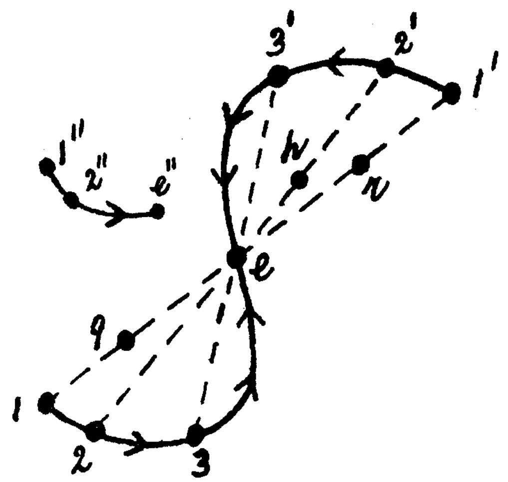

FIG. 1

been determined experimentally and will be more fully discussed later on. We shall call liquids, present at the same moment on both sides of the membrane (*e.g.* 1 and 1′ or 2 and 2′ etc.), "conjugated" liquids; the points representing those liquids are called conjugated points; the lines, uniting two conjugated points (*e.g.* 1.1′ or 2.2′ etc.) are called conjugation lines. Therefore, the conjugation lines of an osmosis path all run through a point e, which represents the composition of the complex and consequently of the final liquid too. Reciprocally every

[2] We here assume that no unmixing into 2 or more liquids will occur in the system.

straight line, going through point e, is a conjugation line; the points of intersection represent two liquids, to be found at a certain moment on both sides of the membrane.

The osmosis path of system (1) starts in Fig. 1 from the points 1 and 1′; its form, however, depends on several other factors, some of which we are going to discuss.

(*a*) The form of the path depends on $n_1:n_1'$ *viz.* on the ratio of the quantities of the liquids, which are brought on both sides of the membrane. For if we alter this ratio, it will be seen from (2) that the position of final point e on line 1.1′ also changes; we imagine this *e.g.* in q (or r). Of course the new osmosis path which must now run through q (or r) has another form than the path running through point e. Consequently an infinite number of paths start from the points 1 and 1′ determined by the ratio $n_1:n_1'$; we are able to prove that these paths touch one another in the points 1 and 1′.

(*b*) The form of the path depends on the direction in which and the velocity with which the substances diffuse through the membrane at any moment; consequently this form also depends on the nature of the membrane used and will, therefore, differ with different membranes. Later on we shall make this clear with some examples and discuss it in connection with other phenomena.

II.

The Experimental Osmosis Path.

If we leave an osmotic system

$$n_1 \times L_1 \mid n_1' \times L_1' \qquad (9)$$

in which the two liquids and their quantities have been absolutely determined, alone, then it will change in a definite way. At a moment t_2 we then have a system

$$n_2 \times L_2 \mid n_2' \times L_2' \qquad (10)$$

in which again the two liquids and their quantities have been completely determined. Consequently the system proceeds along a definite path (1.2.3.e and 1′.2′.3′.e of Fig. 1); we call this the "theoretical" path. If, however, in order to find out the composition of the liquids of (10) we take away a little of these liquids, then we have instead of (10) the new system:

$$(n_2 - q) \times L_2 \mid (n_2 - q') \times L_2' \tag{10a}$$

q and q' represent the quantities, taken away. Although (10) and (10a) consist of the same liquids, they still have another final liquid as a rule. Of course that of (10) is situated in point e; that of (10a) is situated in a point h on the conjugation line 2.2′ (Fig. 1).

In accordance with (5) for e we obtain:

$$e2 : e2' = n_2' : n_2$$

For point h we obtain, however:

$$h_2 : h_{2'} = (n_2' - q') : (n_2 - q)$$

Consequently e and h are different points, unless accidentally:

$$q : q' = n_2 : n_2'$$

System (10) which we no longer have, would, therefore, proceed along the paths 2.3.e and 2′.3′.e; system (10a) which we do have proceeds, however, along the paths 2.h and 2′.h which have not been drawn; consequently both systems proceed along different paths, which touch one another, however, in the points 2 and 2′. (*Cf.* paragraph (a).) Of course the conjugation lines of system (10) all run through point e, those of (10a) through point h.

If we take in (10) *e.g.*, $n_2 = 240$ and $n_2' = 260$, then we have the system:

$$240 \times L_2 \mid 260 \times L_2'$$

If we take away 5 gm. on both sides, then we get:

$$235 \times L_2 \mid 255 \times L_2'$$

For the points e and h we obtain, therefore:

$$e2 : e2' = 260 : 240 = 1.083 : 1$$
$$h2 : h2' = 255 : 235 = 1.085 : 1$$

In Fig. 1 point h must be situated very closely to e; consequently the paths of both systems will practically coincide. As we have to take away a little of the liquids now and then for the experimental determination of a path, we consequently do not define the theoretical path, but a succession of parts of theoretical paths; they pass into one another continually in the points which have been determined experimentally. We call this path the "experimental." The less we change the ratio of the two liquids in taking away little quantities of them, the less the experimental will differ from the theoretical path.

III.

The Path of the Membrane.

As the substances X, Y and W diffuse, the membrane must also contain these three substances; consequently we may say that the membrane contains a liquid, the composition of which changes continually during the osmosis. If in Fig. 1 we represent this liquid by a point, then, during the osmosis, this proceeds along a curve ($1''.2''.e''$ Fig. 1); therefore ,we call this the "path of the membrane."

Consequently we have to distinguish three paths, *viz.* the path of the left side liquid ($1.2.e$), the path of the right side liquid ($1'.2'.e$) and the path of the membrane ($1''.2''.e''$). Of course the final liquid e'' of the membrane generally has another composition than the final liquid e. Therefore, the theoretical and experimental paths of a system depend besides upon the quantity and the composition of the liquid absorbed by the membrane. If, however, we have a small and thin membrane and much liquid, this influence may be neglected; if, however, we have a large or thick membrane, this influence may be very strong. We shall refer to this later on.

IV.

Some Examples.

Now we shall discuss some paths which we have determined in the systems:

$$\text{Water} \mid L_1' \qquad (11)$$

The right side liquid consists of:

$$X = \text{NaCl} \qquad Y = \text{Na}_2\text{CO}_3 \qquad W = \text{H}_2\text{O}$$

On the left side of the membrane is pure water, which, however, takes in X and Y at once and passes into a ternary liquid. The membrane of these systems consisted of a pig's bladder, which had been degreased with ether. The results of the determinations[3] are found in the Tables I–IV. In the first column of I–III we find the number of the determination under t, the time, *viz.* the number of hours after

TABLE I.

	t	X	Y	X	Y
1	0	0	0	6.991	9.021
2	7	1.263	1.423	5.802	7.732
3	19	2.242	2.388	4.992	6.950
4	31	2.739	3.109	4.536	6.452
5	51	3.316	3.533	4.195	6.123
6	91	3.646	4.216	3.877	5.665
7	118	3.682	4.410	3.803	5.437

TABLE II.

	t	X	Y	X	Y
1	0	0	0	6.729	9.057
2	17	1.246	0.387	5.663	8.268
3	29	2.756	1.163	4.557	7.430
4	41	3.589	1.930	3.876	6.856
		——— q		——— q'	
5	69	3.823	2.763	†3.762	6.400
6	101	†4.179	3.547	3.792	5.988
7	143	4.138	4.319	3.843	5.688
8	311	3.934	5.260	3.901	5.378

the beginning of the osmosis. We find in the third and fourth columns under X the amount of NaCl and under Y the amount of Na_2CO_3 of the left side liquid; in the fifth and sixth columns we find the same for the right side liquid. The concentrations have been given in per cent of weight. As the W amount of the liquids follows at once from the X and Y amounts, this has not been given.

[3] They have been done in collaboration with G. M. A. Kayser and L. J. van der Wolk.

System I (*Table I*).—If with the aid of Table I we draw the osmosis path of this system, we get a path such as has been represented schematically by $W2e$ and $1'.2'.e$ in Fig. 2. The left side path We is situated below, the right side path $1'e$ above the conjugation line $W1'$. We see from Table I and Fig. 2 that the X and Y amount of

TABLE III.

	t	X	Y	X	Y
1	0	0	0	9.222	8.976
2	4	0.377	0.087	8.781	8.811
3	12	1.223	0.334	8.024	8.489
4	24	2.366	0.695	7.149	8.056
5	36	3.319	1.054	6.494	7.685
6	54	4.391	1.640	5.852	7.211
7	78	5.212	2.417	5.431	6.702
		——q		——q'	
8	108	†5.666	3.258	5.262	6.206
9	145	5.651	4.051	†5.260	5.903
10	193	5.551	4.660	5.278	5.650
11	240	5.478	5.024	5.308	5.534

TABLE IV.

	X	Y	*Membrane*	*Type*
1 (I)	6.991	9.021	H^a	I
2	7.363	9.194	H^b	I
3	9.238	9.165	H^c	I
4 (II)	6.729	9.057	VI^g	II
5	12.006	7.019	VI^i	II
6 (III)	9.222	8.976	VI^h	III
7	9.227	8.984	VI^d	II or III
8	4.681	10.107	VI^e	II or III

the left side liquid continually increases during the osmosis; that of the right side liquid decreases. Calculating the W amount, we find that the W amount of the left side liquid continually decreases during the osmosis; that of the right side liquid increases.

We may represent the progress of the osmosis still in another way. For this purpose we plot the time t of the osmosis on a horizontal axis

(Fig. 3) with the aid of Table I; on the vertical axis we may plot either the X, the Y or the W amount of the two liquids. If we plot the X amount, we get an $X.t$ diagram such as has been drawn schematically in Fig. 3. The fully drawn curve O.2.3.e obtains for the left side liquid, the dotted curve 1'.2'.3'.e for the right side liquid. The final point e of the two paths is situated at infinite distance; consequently both paths approach one another asymptotically. With the aid of Table I the reader can easily draw the $Y.t$ and $W.t$ diagram of this system himself. We can also summarize the previous considerations in a scheme.

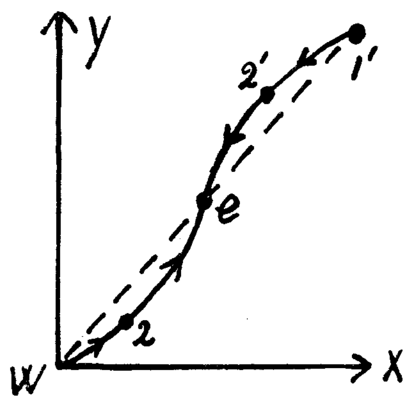

FIG. 2

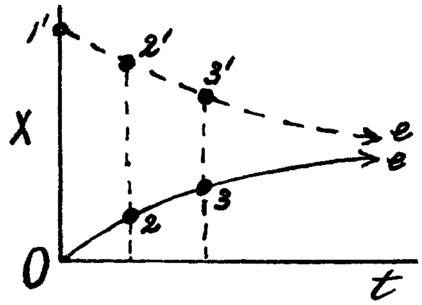

FIG. 3

Scheme I.

X	Y	W	
$\uparrow < \downarrow$	$\uparrow < \downarrow$	$\downarrow > \uparrow$	(12)

This means (*cf.* Paper I) that the left side liquid has a smaller X and Y amount, but a larger W amount than the right side liquid. An arrow pointing upwards indicates that the concentration increases; an arrow pointing downwards indicates that the concentration decreases. This shows therefore, that during the osmosis the X and Y amounts of the left side liquid increases, that of the right side liquid decreases; the W amount of the left side liquid decreases, that of the right side liquid increases. Consequently during the osmosis the liquids change (Paper I) their X, Y and W amounts normally.

System II (*Table II*).—If we draw the osmosis path of this system with the aid of Table II, we get the curves $W.q.5.6.e$ and $1'.q'.5'.6'.e$ of Fig. 4; the $X.t$ diagram has been represented in Fig. 5. For the sake of clearness both figures have been strongly schematised.

It appears from Table II that during the osmosis the X amount (consequently NaCl) of the left side liquid at first increases till the determination marked † (*viz.* 4.179 per cent NaCl) and decreases afterwards. Consequently in the vicinity of $n° = 6$ the left side liquid gets a maximum X amount; we shall plainly say that this maximum coincides with point 6. Consequently the left path $Wq56e$ must have

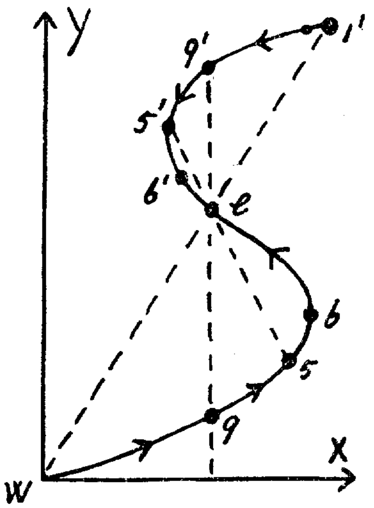

Fig. 4

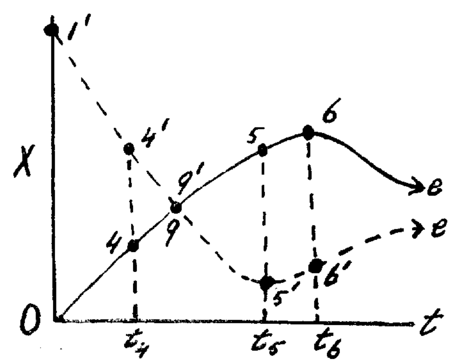

Fig. 5

a vertical tangent in point 6 of Fig. 4; in point 6 of Fig 5 this tangent is horizontal. The X amount of the right side liquid at first decreases till the determination marked † (*viz.* 3.762 per cent NaCl) and afterwards increases. Therefore, in the vicinity of $n° = 5'$ the right side liquid gets a minimum X amount; again we assume that it coincides with point $5'$. The right path $1'\ q'\ 5'\ 6'\ e$ must, therefore, have a vertical tangent in point $5'$ of Fig. 4 and a horizontal tangent in point $5'$ of Fig. 5. It also appears from Table II that between the determinations 4 and 5 the left side and the right side liquids have had the same X amount. This has been indicated in the table by the horizontal lines beside which the letters q and q' have been placed. Consequently in Fig. 4 the conjugation line qeq' is vertical; of course in Fig. 5 q and q' are situated in the point of intersection of the two curves.

It appears from Table II or Fig. 4 that the changes of the Y and W amounts (*viz.* Na_2CO_3 and H_2O) during the total osmosis may be represented by

$$\begin{array}{cc} Y & W \\ \uparrow < \downarrow & \downarrow > \uparrow \end{array} \tag{13}$$

just as in system I the liquids, change their Y and W amounts normally.

The X amount, however, changes in an absolutely different way from that in system I; we see this at once from the $X.t$ diagrams (Figs. 3 and 5) and from the osmosis paths (Figs. 2 and 4). As long as the system remains in the part Wq (and $1'q'$) of its path, the X amount on the left side of the membrane is smaller than on the right side; as during the osmosis it increases on the left side and decreases on the right side, we consequently have the symbol:

$$Wq\ (1'.q') \qquad \uparrow < \downarrow \qquad \text{(Figs. 4, 5)} \tag{14}$$

So in this part of the path the X amount changes as in system I *viz.* normally-normally.

If, however, the left side liquid comes in q and the other consequently in q', both get the same X amount. As this increases on the left side of the membrane and decreases on the right side, we represent it by:

$$q\ (q') \qquad {}^{*}\uparrow = \downarrow{}^{*} \qquad \text{(Figs. 4, 5)} \tag{15}$$

As we may consider the change on both sides of the membrane as abnormal, an asterisk has been placed with both arrows.

So here we have the same X amount on both sides of the membrane; during further osmosis this changes again, becoming equal once more in point e at the end of the osmosis.

When the system is in part $q5$ (and $q'5'$) of its path, then the X amount on the left side is greater than that on the right side. As, however, it is still increasing on the left side and decreasing on the right side, we have the symbol:

$$q5\ (q'5') \qquad * \uparrow > \downarrow * \qquad \text{(Figs. 4, 5)} \tag{16}$$

Consequently the X amount changes abnormally here on both sides.

When the system is in point 5 (and 5′) then the X amount on the right side of the membrane (*viz.* in point 5′) is a minimum; therefore, this X amount does not change in an infinitely small time dt; on the

SCHEME II.

		X	Y	W
Wq	(Wq')	$\uparrow < \downarrow$	$\uparrow < \downarrow$	$\downarrow > \uparrow$
q	(q')	$* \uparrow = \downarrow *$	"	"
$q5$	$(q'5')$	$* \uparrow > \downarrow *$	"	"
5	(5′)	$* \uparrow > \mid *$	"	"
5.6	(5′.6′)	$* \uparrow > \uparrow$	"	"
6	(6′)	$* \mid > \uparrow$	"	"
6.*e*	(6′.*e*)	$\downarrow > \uparrow$	"	"

left side of the membrane it increases, however. We represent this by:

$$5\ (5') \qquad * \uparrow > \mid * \qquad \text{(Figs. 4, 5)} \tag{17}$$

in which the dash indicates that the right side X amount does not change in a time dt.

When the system is in part 5.6 (and 5′.6′) of its path, the X amount increases on both sides. Consequently we have the symbol:

$$5.6\ (5'.6') \qquad * \uparrow > \uparrow \qquad \text{(Figs. 4, 5)} \tag{18}$$

Consequently, the X amount changes abnormally here on the left side and normally on the right side.

If we also consider the system in point 6 (and 6′) and in part 6.*e* (and 6′.*e*) of its path and combine all symbols, we get scheme II. From this we learn among other things the following: At the beginning of the osmosis the X amount of the left side liquid is smaller, afterwards (in q and q') equal, next larger and at the end of the osmosis (point e) again equal to that of the right side liquid. The X amount of the left side liquid increases, beginning at point W as far as 6, and decreases afterwards as far as e. The X amount of the right side liquid decreases, starting from point $1'$ as far as $5'$, and increases afterwards as far as e. The X amount of the left side liquid changes abnormally from q to 6, for it increases, although it is already greater than that of the other liquid. The X amount of the right side liquid changes abnormally from q' to $5'$, for it decreases although it is already smaller than that of the other liquid. On part 5.6 (and $5'.6'$) of the path the X amount increases on both sides of the membrane.

System III (*Table III*).—In many respects this system resembles the preceding one, the following things namely appear from Table III. Between the determinations 7 and 8 the liquids get the same X amount; the X amount of the left side liquid becomes a maximum in the vicinity of the liquid marked † (*viz.* 5.666 per cent NaCl); the X amount of the right side liquid becomes a minimum in the vicinity of the liquid, marked † (*viz.* 5.260 per cent NaCl). For all that, there is a great difference between both systems. For in system II, first the right minimum occurs and afterwards the left maximum; during the osmosis in system III we have just the reverse, for here the left maximum occurs first and afterwards the right minimum. Consequently, system III may indeed be represented schematically by Figs. 4 and 5, if we interchange the places of maximum and minimum with respect to one another. The scheme of this system, which the reader may easily deduce himself, contains also symbols different from those in scheme II.

Besides the paths discussed above, we have determined those of other systems:

$$\text{Water} \mid L_1' \tag{19}$$

In Table IV the composition of the liquid L_1' of eight systems is found. The complete tables of the systems 1 (I), 4 (II) and 6 (III) are found in Tables I, II and III respectively; if any one should be interested in the other tables, I shall be pleased to forward them. The form of the path has been indicated under "type"; I means a form as in system I, etc. As in II and III, the systems 7 and 8 have a maximum in their left side path and a minimum in their right side path; as they occur, however, almost at the same time, it is difficult to say whether they belong to II or to III.

In these systems we have used two membranes H and W (no attention should be paid to the small letters a, b, etc. in Table IV): both consisted of a piece of pig's bladder; H, however, was of another bladder than bladder VI. It appears from Table IV that the paths of the eight systems (19) belong to three different types; consequently we put the question: what is the cause?

Of course the form of the path depends on the composition of liquid L_1', consequently on the position of point 1′ in the diagram. However it appears from the table that L_1' has almost the same composition in the systems 1 and 4: yet the type of both paths is different. We see the same thing for the systems 3 and 6 and also for 3 and 7. We have already seen that the form of the path depends on $n_1:n_1'$; this influence, however, has been eliminated here as much as possible.

As has been discussed above, the form of the path, however, depends also on the membrane. It now appears from Table IV that type I occurs in all systems (*viz.* 1–3) in which bladder H has been used and type II or III in all systems in which bladder VI has been used. Consequently this makes it probable that the cause of this phenomenon must be looked for in a difference between the bladders H and VI.

This shows that the nature of the membrane influences the form of the path; later on we shall see this confirmed by other examples. If we bear in mind that all sorts of influences (*e.g.* the action of the diffusing substances, age, hysteresis, etc.) may modify the nature of the membrane (permeability, adsorptive capacity, etc.) it becomes clear that, even when using apparently the same membrane, the type of the osmosis path may differ.

The question then arises in which direction do these substances X, Y and W diffuse through the membrane? Although we shall not discuss this question until a later communication I wish to emphasize the point that great care must be used. Let us take *e.g.* scheme II or Table II which obtains for system II. We see from them that the Y amount of the left side liquid increases perpetually whereas that of the right side liquid decreases. If we should deduce from this that during the osmosis Y (Na_2CO_3) diffuses perpetually towards the left, our conclusion would not be based on a single ground; it may be wrong as well as right.

This appears at once when we consider *e.g.* the change of the X

amount on part 5.6 of the path. We see that this now increases on both sides of the membrane. For the change in concentration of a substance not only depends on the direction in which this substance passes through the membrane, but also on the directions of the other substances. The X and Y amounts of the liquids change when nothing but water diffuses. (*Cf. e.g.* normal and abnormal changes in scheme 24 of Paper I.) Consequently from the vertical arrows no conclusion may be drawn with respect to the directions in which the substances pass through the membrane. As we shall see later on, we can only deduce them by considering the synchronous changes in concentration of the three substances.