The chloroform solution did not depose any crystals till the end of the reaction and they only gradually appeared after standing for some time. The melting point of this tetrabromide was 74° and on further recrystallisation 96°.

The tetrabromide melting at 174° could not be demonstrated.

Samples of the glycols *A* and *B* were subjected to fractional destillation. The main fraction showed the following constants:

	Glycol A	Glycol B	
B.P.$^{45 mm}$	125°	125°	
d_{15}^{18}	1.027	1.016	
n_D^{18}	1.4822	1.4775	
MR_D	31.66	31.73	Calc. for $C_6H_{10}O_2|\overline{2}$ 32.
M.P.	+ 10°	— 40°	

A further investigation of the glycol is to follow.

Chemistry. — *Osmosis in systems consisting of water and tartaric acid.* I. By F. A. H. SCHREINEMAKERS and J. P. WERRE.

(Communicated at the meeting of January 30, 1932.)

Introduction.

We imagine the composition of a liquid, containing the substances *W* (water) and *X*, represented in the well-known way by a point *a* of the line *WX* (figs. 1 and 2). If we bring an invariant membrane[1]), absorbing both substances, into this liquid *a*, then it will get a definite *W*- and *X*-amount, which we represent by the length of the line *aa'* and *aa''* (fig. 1). If we give all compositions, beginning with pure *W* (water) and ending with the pure substance *X*, to this liquid *a*, then point *a'* will proceed along a curve *W'a'X* and point *a''* along a curve *Wa''X'*, which curves we call the *W*- and *X*-curves of the membrane.

We may divide these absorption-diagrams into four groups, depending on the *W- and X*-curves having a maximum yes or no [figs. 1—4 of these Proceedings **32**, 837 (1929)].

I. Neither of the two curves has a maximum (fig. 1 l.c.).
II. Only the *W*-curve has a maximum (fig. 2 l.c.).
III. Only the *X*-curve has a maximum (fig. 3 l.c.).
IV. Both curves have a maximum (fig. 4 l.c.).

In fig. 1 of this communication we find a diagram I, in fig. 2 a diagram II; in the last case, however, only the *W*-curve has been drawn, the *X*-curve, not drawn, has a shape as given in fig. 1.

1) F. A. H. SCHREINEMAKERS, Rec.-Trav. Chim. des Pays-Bas, **50**, 883 (1931).

We now shall say that an osmotic system belongs to type I (II, III or IV), when we are able to describe and deduce its osmosis with the aid of the sluice $D.T.$ of diagram I (II, III or IV).

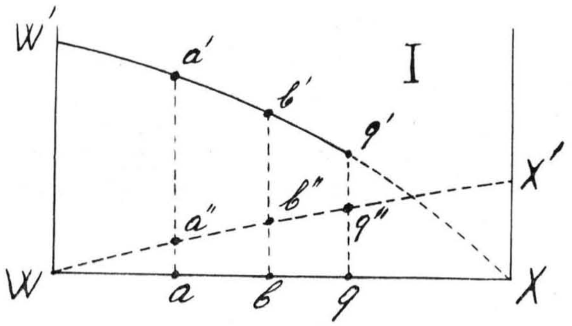

Fig. 1.

Of course it does not follow from the above that the membrane of an osmotic system, belonging e.g. to type I, will now also have a W- and an X-curve as in diagram I; this is possible, indeed, but not necessary [1]).

We may attach also quite another meaning to the W- and X-curve of these diagrams, in which case we no longer pay attention to the absorption by the membrane and consequently not to its sluice $D.T.$ either.

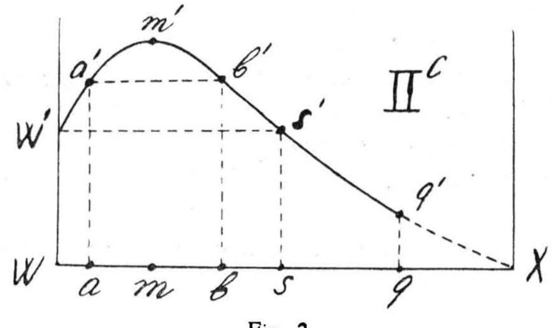

Fig. 2.

To every liquid of the line WX namely belongs a point of the W- and a point of the X-curve; we shall call these points the W- and X-point of this liquid; e.g. to liquid a (fig. 1) belong the W-point a' and the X-point a'', to liquid b the W-point b' and the X-point b''. As $aa' > bb'$ we shall say that liquid a has a higher W-point than liquid b; as $aa'' < bb''$ we shall say that liquid a has a lower X-point than liquid b. Besides we shall also say now:

a diagram represents the osmosis of a system schematically, when the phenomena occurring with the osmosis can be described qualitatively and deduced with the aid of the rule:

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1) F. A. H. SCHREINEMAKERS, l. c.

the water (the substance X) diffuses from the liquid with the higher towards the liquid with the lower W-point (X-point); when the W-points (X-points) of two liquids are situated at the same height, no water (X) diffuses.

Here also we shall say now:

an osmotic system belongs to type I (II, III or IV) when we are able to describe its osmosis with the aid of diagram I (II, III or IV).

The W-and X-curves of the diagrams have now been given a meaning which is no longer connected with the absorption by the membrane; it also enables us, however, to get a clearer view of the phenomena occurring with the osmosis.

We now take an osmotic system

$$L\,(W + \textit{tartaric acid}) \mid L'\,(W + \textit{tartaric acid}) \quad . \quad . \quad . \quad (1)$$

in which the liquids consist of water and tartaric acid. The phenomena which may occur with the osmosis in this system, depend not only upon the concentration of the two liquids, but also upon the nature of the membrane. It appeared namely from our experimental investigation:

1. if we bring a membrane of cellophane into system (1), the system belongs to type I;
2. if we bring a membrane of pig's bladder into system (1), the system belongs to type II.

If in figs 1 and 2 we represent the solution, saturated with solid tartaric acid by point q, then only the parts of the W- and X-curves, situated on the left side of the line qq', represent stable states; the stable part $W'q'$ of the W-curve has been fully drawn in both figures; the metastable part $q'X$ shown in a dotted line, may henceforth be left out of consideration.

Systems with a membrane of cellophane. Type I, fig. 1.

We now take the osmotic system

$$L\,(W + X) \mid L'\,(W + X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2^a)$$

in which the tartaric acid has been represented by X: for the sake of concentration we shall in this and in the following systems place the liquid with the smaller X-amount on the left side and consequently that with the larger X-amount on the right side of the membrane.

If in figs. 1 and 2 we represent these liquids by points of the line WX, then L will consequently always be situated on the left side of L'.

If we bring a membrane of cellophane into this system, then, as we shall see later on, we are able to deduce and describe all phenomena, found with the osmosis in this system, with the aid of fig. 1; consequently this system belongs to type I.

We now imagine the liquids L and L' of this system represented in fig. 1 by the points a and b. As $aa' > bb'$, it follows that liquid L has a higher W-point than liquid L'; we indicate this by $w > w'$. As $aa'' < bb''$, it follows that liquid L has a lower X-point than L'; we represent this by $x < x'$. Now we shall represent (2a) by:

$$\left.\begin{array}{c|c|c} L\,(W+X) & \begin{array}{c} w > w' \\ x < x' \end{array} & L'\,(W+X) \\ \leftarrow X & \rightarrow W & \end{array}\right\} \quad . \; . \; . \; . \; . \; . \quad (2^b)$$

As is apparent from fig. 1, this obtains not only for the liquids a and b, but for any liquid L and L', provided that, as has been assumed above, liquid L has a smaller W-amount than liquid L'.

As the water diffuses from a liquid with the higher-towards a liquid with the lower W-point, the water must consequently always flow through the membrane →. As the substance X also flows from a liquid with the higher-towards a liquid with the lower X-point, the substance X must consequently always diffuse ←. So the water and the substance X will always diffuse according to the arrows in (2b).

Consequently the water always diffuses from the liquid with the greater towards the liquid with the smaller W-amount; the substance X (viz. the tartaric acid) diffuses from the liquid with the greater towards the liquid with the smaller X-amount; consequently the two substances here diffuse congruently and positively. In our next communication we shall show that the water can also diffuse incongruently and negatively, when the cellophane is replaced by a pig's bladder.

Systems in which the left-side liquid is invariant.

As a special case of (2a) or (2b) we first consider the system

$$\left.\begin{array}{c|c} inv.\ (Water) & L'\,(W+X) \\ \leftarrow X & \rightarrow W \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

in which on the left side of the membrane we have pure water, which during the entire osmosis is renewed continuously or at short intervals, so that we may practically consider the state on the left side of the membrane as invariant.

It appears from the arrows that the water will now always diffuse → namely from the pure water towards the solution; the tartaric acid diffuses ← namely from the solution towards the pure water.

We now take first an osmotic system, in which at the beginning of the osmosis the variable liquid L' of system (3) contains in procents of weight:

$$43.213\ \%\ W + 56.787\ \%\ \textit{tartaric acid}$$

we represent this system by:

$$inv. (Water) \mid L' (56.787 \, {}^0/_0 \, X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The data for this system are found in table A. In the first column we find the numbers of the successive determinations, in the second column the time, namely the number of hours passed after the beginning of the osmosis; in the third column we find the composition of the invariant liquid L, consisting of pure water during the entire osmosis and having, therefore, an X-amount $= 0$ %; in the last column we find the X-amount of the variable liquid L'.

In the fourth column we find sub X the number of grams of X and in the fifth column sub W the number of grams of water, which have passed through the membrane between two successive determinations; the arrows indicate the direction, in which these quantities have diffused. We see that these directions correspond with those of the arrows in system (3).

It appears from Nos 1 and 2 that the X-amount of the variable liquid L' had after 6 hours decreased from 56.787 to 52.229 % and that at this time 2.975 gr. of X had diffused towards the left and 18.020 gr. of water towards the right.

It appears from N⁰. 3 that the X-amount of the variable liquid had after the beginning of the osmosis decreased to 46.395 % in 15 hours; it follows

TABLE A. System (4).

N⁰.	t	${}^0/_0$ X of the inv. liq. L	Diffused		${}^0/_0$ X of the var. liq. L'
			gr. X	gr. W	
1	0	0			56.787
			←	→	
2	6		2.975	18.020	52.229
3	15		4.508	26.380	46.395
4	24		4.256	23.242	41.895
5	36		4.942	27.061	37.321
6	48		5.444	25.213	33.421
7	65		6.678	31.806	29.132

from Nos 2 and 3 together that between these two determinations (consequently in $15 - 6 = 9$ hours) 4.508 gr. of X had diffused towards the left and 26.380 gr. of water towards the right.

From this follows also that in 15 hours counting from the beginning of the osmosis

$$2.975 + 4.508 = 7.483 \; gr. \; X \; (tartaric \;\; acid)$$

in all had diffused towards the left and

$$18.020 + 26.380 = 44.400\ gr.\ W\ (Water)$$

in all towards the right.

It follows from the last determination N⁰. 7 that the X-amount of the variable liquid L' had decreased to 29.132 % in 65 hours counting from the beginning of the osmosis; we find that now 28.803 gr. of X in all had diffused towards the left and 151.722 gr. of W towards the right.

As is shown by table A, the osmosis of system (4) stopped, when the variable liquid L' still contained 29.132 % of tartaric acid; in order to become acquainted with the subsequent course of the osmosis, we now take the system

$$inv.\ (Water) \mid L'\ (34.628\ \%\ X) \quad \ldots\ldots \quad (5)$$

in which at the beginning of the osmosis the variable liquid contains

$$65.372\ \%\ W + 34.628\ \%\ tartaric\ acid.$$

From the determinations [1]), which were carried on until the variable liquid contained only 0.008 % of X, it now appears that also during this entire osmosis the substance X and the water diffuse according to the arrows of system (3).

From this table (l.c.) it appears among other things that the X-amount of the variable liquid had decreased to 31.576 % in 9 hours counting from the beginning of the osmosis and that then 4.726 gr. of X had diffused towards the left and 19.082 gr. of water towards the right.

In 160 hours the X-amount of the variable liquid had decreased to 7.978 %, then 51.923 gr. of X had diffused towards the left and 197.645 gr. of water towards the right.

In 1053 hours the X-amount of the variable liquid decreased to 0.008 % and 73.801 gr. of X had in all diffused towards the left and 311.062 gr. of W towards the right.

We now take the osmotic system

$$inv.\ (Water) \mid L'_q\ (W + X) + solid\ X \quad \ldots\ldots \quad (6)$$

in which the right side liquid has been saturated with solid tartaric acid; in fig. 1, therefore, it is represented by the point q.

As for this system the arrows of system (2b) or (3) obtain also, the liquid L' will give off the substance X and take in water; so in this

[1]) J. P. WERRE. Diss. Leiden 1931, table VI, pag. 33; this table in which 22 determinations occur and in which the tartaric acid has been indicated by Z, has practically been arranged in a similar way as that of table A.

system two factors cooperate to cause the disappearance of the solid substance X; as soon as all the solid substance has disappeared, this system passes into system (3).

If in system (6) we omit the liquid, we get a system

$$inv.\,(Water) \mid solid\ tartaric\ acid \quad \ldots\ldots \quad (7)$$

Let us now imagine that at a certain moment a very small quantity of water diffuses, then on the right side some saturated solution will form. As system (7) then passes into (6), the water-diffusion will now, as we saw before, continue towards the right and the substance X will diffuse towards the left. From this it follows, as we have also learned experimentally, that the solid tartaric acid in system (7) will deliquesce and dissolve.

Systems in which the right side liquid is invariant.

As an other special case of system (2a) or (2b) we now take a system

$$\left.\begin{array}{ll} L\,(beg.\ Water) & \mid\ inv.\,L'\,(W+X) \\ \leftarrow X & \rightarrow W \end{array}\right\} \quad \ldots\ldots \quad (8)$$

in which an invariant liquid is found this time on the right side of the membrane. On the left side of the membrane is a variable liquid L, consisting at the beginning of the osmosis of pure water. In order to determine the osmosis in such a system (8), we took the system:

$$L\ (beg.\ Water) \mid inv.\ L'_q\,(W+X) + solid\ X \quad \ldots \quad (9)$$

in which the liquid L' is saturated with solid X; if we take care that a large quantity of solid tartaric acid is present all the time, then liquid L' will be practically invariant. This liquid represented in fig. 1 by point q contains

$$\pm\, 42.5\ \%\ \text{of}\ W\ \text{and}\ \pm\, 57.5\ \%\ \text{of}\ tartaric\ acid.$$

We now represent this system by:

$$L\,(beg.\ Water) \mid inv.\ L'_q\,(57.5\ \%\ X) \quad \ldots\ldots \quad (10)$$

The data, concerning the osmosis in this system are found in table B, which has been arranged in a similar way as that of table A; the liquid L (third column) now is variable, however, and the liquid L' (last column) invariant.

It appears from the arrows of this table B that the substance X and the

TABLE B. System (10).

N⁰.	t	$^0/_0$ X of the var. liq. L	Diffused		$^0/_0$ X of the inv. liq. L'
			gr. X	gr. W	
1	0	0			± 57.5
			←	→	
2	3	0.425	1.611	8.122	
3	8	1.145	2.455	13.431	
4	16	2.397	3.745	18.115	
5	28	5.089	6.762	33.468	
6	40	7.651	5.345	26.498	
7	49	8.684	2.988	16.361	
8	73	12.170	8.620	47.951	
9	93	15.149	5.929	34.101	
10	111	17.633	4.148	24.577	
11	131	21.240	5.075	30.348	
12	164	28.858	7.252	50.958	
13	204	37.301	4.495	41.170	
14	248	40.325	2.391	28.547	
15	291	43.029	2.464	24.156	
16	362	46.219	1.600	26.508	
17	457	49.853	1.811	26.083	
18	625	52.998	0.050	21.141	
19	888	55.631	1.632	14.512	

water diffuse also in this system during the entire osmosis in the way indicated by the arrows in system (2*b*).

From this table *B* it besides appears among other things that the X-amount of the variable liquid L, consisting of pure water at the beginning of the osmosis, had increased to 0.425 % after 3 hours and that then 1.611 gr. of X had diffused towards the left and 8.122 gr. of water towards the right.

After 111 hours the X-amount of the variable liquid had increased to 17.633 % and 41.603 gr. of X had diffused towards the left and 222.624 gr. of water towards the right.

After 888 hours the X-amount of the variable liquid had increased to 55.631 % and had consequently almost come up to that of the saturated solution L'; then 68.373 gr. of X had gone towards the left and 486.047 gr. of water towards the right.

The diffusing mixture.

Above we have seen that in system (2*a*) or (2*b*) and in all systems deduced from them the substance X and the water diffuse during the entire osmosis in the way indicated by the arrows in (2*b*). We now represent this by

$$\leftarrow \alpha . X \qquad \rightarrow \gamma\, W \qquad \text{. . . . . (11)}$$

in which α and γ indicate the small quantities of X and W, flowing through the membrane between the moments t and $t+dt$. It appears from the tables A, B and VI (l.c.) that during the entire osmosis $\alpha < \gamma$.

So in this time dt the quantity of the left side liquid L decreases with a positive quantity $\gamma - \alpha$ and that of the right side liquid L' increases with the same quantity $\gamma - \alpha$. From this follows that we now may say also: liquid L gives off and liquid L' takes in $\gamma - \alpha$ quantities of a mixture with the composition:

$$x_0\, X + (1 - x_0)\, W \qquad \text{. . . . . (12)}$$

in which

$$x_0 = \frac{-\alpha}{\gamma - \alpha} \text{ and } 1 - x_0 = \frac{\gamma}{\gamma - \alpha} \qquad \text{. . . . . . (13)}$$

so that x_0 is negative and consequently $1 - x_0$ positive, and larger than 1; before [1]) we have called this mixture the diffusing mixture.

We can also represent the composition of this diffusing mixture by a point d, not drawn in fig. 1, of the line WX. As, however, this mixture is not a liquid existing in reality (this mixture namely has a negative X-amount and a W-amount larger than 1), this point will of course not be situated between the points W and X; it is easy to find that this point d must be situated to the left of point W, namely somewhere on the prolongation of line WX. The length of line dW then represents the negative X-amount and the length of line dX the positive W-amount of this mixture.

Later on we shall refer again to the diffusing mixture and its movement during the osmosis.

(To be continued.)

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[1]) F. A. H. SCHREINEMAKERS. Verslagen K. Ak. v. W., **36**, 1103 (1927). These Proceedings **30**, 1095 (1927).