Chemistry. — *On absorption and osmosis.* II. By F. A. H. SCHREINEMAKERS and C. L. DE VRIES.

(Communicated at the meeting of April 29, 1933).

I. *The osmotic system water* $+Na_2CO_3$ *with a membrane of pig's bladder.*

We imagine in the osmotic system

$$L\,(W+X)\,|\,L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $W=$ water and $X=Na_2CO_3$, a membrane of pig's bladder and the two liquids placed in such a way always that the left-side liquid always has a smaller X- and consequently a greater W-amount than the right-side liquid. As will appear from the experimental investigation to be discussed later on, the osmosis will then always proceed according to the D.T.

$$\leftarrow X \quad \rightarrow W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

no matter what concentrations the liquids L and L' may have.

As the substance X (viz. the Na_2CO_3) diffuses $\leftarrow$, namely from the liquid with the greater-towards that with the smaller X-amount, X always diffuses in congruent and positive direction; the same obtains for the water, which always diffuses $\rightarrow$, namely from the liquid with the greater-towards that with the smaller W-amount. As both substances now diffuse in congruent direction, (2), therefore, will represent the congruent D.T.

We shall now discuss some of the experimental investigations of system (1).

1. First we take the osmotic system

$$L\,(beg.\ Water)\,|\,L'\,(beg.\ 11.831\ {}^0\!/_0\ X) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which, at the beginning of the osmosis, there is pure water on the left side and on the right side a liquid, containing 11.831 % of Na_2CO_3.

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 X-amount of the liquid L and in the last column the X-amount of the liquid L'.

It appears from Nos 1 and 2 that in 11 hours the X-amount of liquid L has increased from 0 % to 0.424 % and of liquid L' decreased from 11.831 % to 10.518 %; the further determinations show that the X-amount of liquid L continuously increases and that of liquid L' continuously decreases. After 339.3 hours the two liquids have almost the same X-amount (viz. 5.030 % and 5.061 %) and consequently the osmosis is practically over.

TABLE A. System (3).

N⁰.	t in hours	% X of liq. L	Diffused according to the determinations				% X of liq. L'
			of liq. L		of liq. L'		
			gr X	gr W	gr X	gr W	
1	0						11.831
			←	→	←	→	
2	11.0	0.424	1.629	26.817	1.624	26.659	10.518
3	23.5	0.935	1.596	24.777	1.588	24.830	9.423
4	35.8	1.470	1.897	20.697	1.337	20.047	8.452
5	54.1	2.265	1.558	22.992	1.533	22.798	7.461
6	80.2	3.340	1.615	22.449	1.584	22.452	6.570
7	121.7	4.494	1.304	18.087	1.366	18.121	5.890
8	192.0	4.857	0.847	11.595	0.885	11.490	5.290
9	339.3	5.030	0.367	4.730	0.338	4.633	5.061

Successive determinations of the quantity and the composition of liquid L enable us to deduce how much X and how much water has been taken in or given off by this liquid L between two successive determinations; we find these diffused quantities in the 4th and 5th columns (sub : of liquid L) ; the arrows indicate the direction in which these substances have diffused.

From Nos 1 and 2 it appears that in 11 hours after the beginning of the osmosis 1.629 grs. of X have diffused ← and 26.817 grs. of water →. From Nos 2 and 3 it appears that between these two determinations (consequently in 23.5—11 = 12.5 hours) 1.596 grs. of X have diffused ← and 24.777 grs. of W →. From this also follows that in 23.5 hours counting from the beginning of the osmosis 1.629 + 1.596 = 3.225 grs. of X had diffused ← and 26.817 + 24.777 = 51.594 grs. of water →. Further determinations show that during the entire osmosis the substance X has diffused ← and the water →, so that the osmosis has taken place according to the D.T. (2).

The quantities of X and W that have diffused may also be deduced from the successive determinations of the quantity and composition of liquid L'; from the results of these determinations, to be found in the 6th and 7th columns, also follows that the osmosis has taken place according to the D.T. (2).

Comparing the quantities of X that have diffused in the 4th column with those of the 6th column, we note small differences; this obtains also for the quantities of water diffused in the 5th and 7th columns. If, however, we take the experimental difficulties of these determinations into consideration and the change in the absorption of X and W by the membrane, so that during the osmosis it can also take in or give off small quantities of X and W, then it is clear that small differences will occur always. This change in the absorption by the membrane results from the change in the concentrations of the two liquids, with which it is in contact during the osmosis; of course a change in the nature of the membrane can also play a part here (comp. Comm. I).

Besides system (3) discussed above, the three following systems

$$L\,(beg.\ 0.491\ \%\ X)\ |\ L'\,(beg.\ 4.678\ \%\ X) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$L\,(beg.\ 3.912\ \%\ X)\ |\ L'\,(beg.\ 7.822\ \%\ X) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$L\,(beg.\ 7.825\ \%\ X)\ |\ L'\,(beg.\ 11.883\ \%\ X) \quad . \quad . \quad . \quad . \quad (6)$$

have also been examined. It appeared from the experimental investigations [1]) that here also during the entire osmosis the substance X and the water run through the membrane congruently and positively and consequently according to D.T. (2).

2. We now take the osmotic system

$$inv.\,(Water)\ |\ L'\,(beg.\ 11.878\ \%\ X) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which only one variable liquid, viz. L', containing 11.878 % of Na_2CO_3 at the beginning of the osmosis; the other liquid consists of pure water which during the osmosis is being renewed at short intervals, so that we may consider the state on the left side of the membrane as practically invariant.

The data for this system are found in table B, in which the 1st, 2nd, 3rd and last columns have the same meaning as in table A; as, however, the left-side liquid is invariant, its composition remains 0 % of X during the entire osmosis. From the last column it appears that the X-amount of the variable liquid decreases continuously and has come down to 0.081 % after 674.2 hours (or about 28 days).

As system (7) contains only one variable liquid, the quantities of X and W that have diffused and the direction in which they have passed through

---

[1]) C. L. DE VRIES, Dissertation, Leiden 1932, Tables XXVII, XXVIII and XXIX.

the membrane, can only be deduced from successive determinations of the quantity and composition of the variable liquid L'. We find these quantities diffused in the 4^{th} and 5^{th} columns; the arrows indicate the direction in which these quantities have diffused.

TABLE B. System (7).

N⁰.	t in hours	$^0/_0$ X of the inv. liq.	Diffused		$^0/_0$ X of the var. liq.
			gr X	gr W	
1	0	0	←	→	11.878
2	7.6	—	0.034	10.889	10.954
3	18.1	—	1.655	17.920	9.934
4	32.1	—	2.198	27.238	8.617
5	46.1	—	1.989	25.075	7.550
6	64.4	—	2.264	28.302	6.468
7	89.4	—	2.899	34.834	5.266
8	116.7	—	2.597	32.130	4.300
9	147.2	—	2.425	31.388	3.471
10	183.8	—	2.405	34.005	2.670
11	233.8	—	2.414	40.479	1.772
12	294.2	—	0.766	41.894	1.097
13	345.7	—	0.971	35.020	0.738
14	411.2	—	0.791	44.816	0.442
15	485.2	—	0.486	47.845	0.257
16	557.2	—	0.251	45.434	0.156
17	674.2	—	0.184	53.676	0 081

It appears from these determinations that during the entire osmosis the substance X has diffused ← and the water →; so both substances have continuously passed through the membrane according to the D.T. (2).

The osmotic system

$$inv.\,(Water)\,|\,L'\,(beg.\ 2.964\ ^0/_0\ X)\ .\ .\ .\ .\ .\ .\ \quad (8)$$

was examined successively four times for reasons that will be entered into later on; it appears from the investigations[1]) that here also the osmosis continuously took place according to the D.T. (2).

[1]) C. L. DE VRIES, l.c. Table XXXII—XXXV.

In the osmotic system

$$inv.\,(Water)\,|\,L'\,(W+X)+solid\,Na_2\,CO_3\,.\,10\,H_2O \quad . \quad . \quad (9)$$

liquid L' is in equilibrium with the solid hydrate $Na_2CO_3 \,.\, 10\,H_2O$. During the osmosis this solid hydrate disappeared and liquid L', which at first had been saturated with the hydrate, became unsaturated. It appeared from the investigations [1]) that the Na_2CO_3 and the water had again passed through the membrane during this osmosis according to the D.T. (2).

In the osmotic system

$$inv.\,(Water)\,|\,solid\,Na_2\,CO_3\,.\,10\,H_2O \quad . \quad . \quad . \quad . \quad . \quad (10)$$

only the solid hydrate $Na_2CO_3 \,.\, 10\,H_2O$ is present on the right side of the membrane. At an experimental investigation, in which 196.5 grs. of this solid hydrate were taken, all solid substance had disappeared after 108 hours and on the right side an unsaturated liquid had formed. Investigation [2]) showed that here also the osmosis had taken place according to D.T. (2).

3. We now take the osmotic system

$$L\,(beg.\ Water)\,|\,inv.\,L'\,(11.485\,^0/_0\,X) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which on the right side an invariant liquid is present now, containing 11.485 % of Na_2CO_3; on the left side is a variable liquid L, consisting at the beginning of the osmosis of pure water. The data for this system are found in table C, which has been arranged in a similar way as table B.

From this it appears that the X-amount of the variable liquid, consisting of pure water at the beginning of the osmosis, increased continuously and had run up to 11.203 % after 548.3 hours. It appears from the direction of the arrows in the 4^{th} and 5^{th} columns that also in this system the osmosis had taken place according to D.T. (2).

The same obtains, as is clear from our investigations [3]) also for the osmotic system

$$L\,(beg.\ Water)\,|\,inv.\,L'\,(W+X)+solid\,Na_2\,CO_3\,.\,10\,H_2O \quad . \quad (12)$$

in which liquid L' was continuously kept saturated and consequently invariant by the presence of a sufficient quantity of solid $Na_2CO_3 \,.\, 10\,H_2O$.

II. *The sluice and the real diffusion-type.*

When we bring the membrane of the osmotic system

$$L\,(W+X)\,|\,L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

[1]) C. L. DE VRIES, l.c. pg. 53.
[2]) C. L. DE VRIES, l.c. pg. 54.
[3]) C. L. DE VRIES, l.c. Table XXVI.

TABLE C. System (11).

N⁰.	t in hours	$^0/_0$ X of the var. liq.			$^0/_0$ X of the inv. liq.
			gr. X	gr W	
1	0	0	←	→	11.485
2	10.0	0.300	1.082	24.396	—
3	33.8	1.236	2.526	50.218	—
4	58.0	2.530	2.228	45.390	—
5	82.5	4.167	1.698	36.619	—
6	109.0	4.851	1.463	31.663	—
7	150.5	5.953	1.867	42.263	—
8	201.5	7.250	1.651	39.651	—
9	264.7	8.629	1.342	33.143	—
10	338.3	9.796	0.837	23.280	—
11	434.3	10.665	0.458	15.146	—
12	548.3	11.203	0.388	7.217	—

into liquid L, it will get a definite X- and W-amount in it, which we shall call x and w; if we bring this membrane into liquid L', then it will get an X- and a W-amount x' and w' in it.

If now $x < x'$ and $w > w'$, we represent system (13): by

$$L\,(W+X)\left|\begin{array}{c} x < x' \\ w > w' \end{array}\right| L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If we make a sluice-arrangement [1]) of this membrane, we see that the substance X will diffuse ← and the water →; consequently the sluice-D.T. of (13) is:

$$\leftarrow X \quad \rightarrow W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If now not only $x < x'$ but also $w < w'$, we represent system (13) by:

$$L\,(W+X)\left|\begin{array}{c} x < x' \\ w < w' \end{array}\right| L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The sluice D.T. of this system then will be:

$$\leftarrow X \quad \leftarrow o * W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

From this it appears that we may say: the substance X (the water)

[1]) F. A. H. SCHREINEMAKERS, These Proceedings **32**, 1152 (1929) and following communications. Recueil Trav. Chim. Pays-Bas **50**, 221 and 883 (1931).

diffuses in the sluice D.T. from the liquid in which the membrane would get the greater X-amount (W-amount), towards the liquid in which the membrane would get the smaller X-amount (W-amount).

From this it follows that the sluice D.T. of a system is being determined by the X- and W-amount the membrane would get in the liquids L and L'; so it depends on the X- and W-curve of the membrane, which, as we have seen previously (Comm. I, figs. 1, 2 and 3), can have different shapes.

In order to apply these considerations to an example, we shall in connection with our further discussions take the osmotic system:

$$inv. \, (Water) \mid L' \, (W + X) \quad \ldots \ldots \quad (18)$$

We now first imagine that the X- and W-curves of the membrane have a shape like those in fig. 1 (Comm. I), which we shall call diagram I. As the membrane in the water will always get a smaller X- and a greater W-amount than in liquid L', the sluice D.T. will be

$$\leftarrow X \quad \rightarrow W \quad \ldots \ldots \quad (19)$$

no matter what composition liquid L' may have.

If we now suppose in fig. 2 (Comm. I) an X-curve like the one in fig. 1 (Comm. I), we shall call this figure diagram II. If we now take liquid L' of system (18) somewhere between the points W and s, then the membrane will get a smaller W-amount in the water than in liquid L'. During the entire osmosis the sluice D.T. will now be:

$$\leftarrow X \quad \leftarrow o * W \quad \ldots \ldots \quad (20)$$

If, however, we take liquid L' somewhere between s and X, the membrane will get a greater W-amount than in liquid L'; we then once more get the sluice D.T. (19).

As, however, the X-amount of liquid L' decreases continuously during the osmosis and liquid L', therefore, moves towards point W along the line WX of the diagram, the sluice D.T. (19) will at a certain moment of the osmosis pass into (20) again.

Limiting ourselves to solutions of liquid L' of which the concentration is not too high, it follows:

$$\textit{sluice D. T. of diagram I} \quad \leftarrow X \quad \rightarrow W \quad \ldots \quad (21)$$

$$\textit{sluice D. T. of diagram II} \quad \leftarrow X \quad \leftarrow o * W \quad \ldots \quad (22)$$

If we leave an osmotic system alone, (i.e. if we do not make a sluice arrangement of the membrane), the substances will diffuse according to some D.T., which we shall call the real D.T. of this system. It is clear that during the osmosis a system can successively have different real D.T.'s also.

We now may put the question whether the real D.T. of a system is the same or not the same as the sluice D.T. From theoretical considerations [1]) it follows that the two D.T.'s may be identical, but that this is not necessarily the case.

In order to illustrate this with some examples, we imagine in system (18):

$$X = \textit{tartaric acid, membrane of cellophane} \quad . \quad . \quad . \quad (23)$$

From Chapter V (Comm. I) it now appears that the X- and W-curves of this system may be represented by diagram I, so that the sluice D.T. resembles that in (21); from the osmosis it appears that the real D.T. is identical [2]).

We now take in system (18)

$$X = \textit{tartaric acid, membrane of pig's bladder} \quad . \quad . \quad . \quad (24)$$

or

$$X = \textit{succinic acid, membrane of pig's bladder} \quad . \quad . \quad . \quad (25)$$

It now appears from Chapters III and IV (Comm. I) that the X- and W-curves of each of these two systems can be represented by diagram II, so that the sluice D.T. is the same as in (22). It appears from the osmosis that the real D.T. is identical.

We now take in system (18):

$$X = Na_2CO_3, \textit{ membrane of pig's bladder} \quad . \quad . \quad . \quad (26)$$

From Chapter II (Comm. I) it now appears that it depends on the prehistory of the bladder whether the X- and W-curves can be represented either by diagram I or by II; so it also depends upon the prehistory of the bladder whether the sluice D.T. will be the same as in (21) or as in (22). From the experimental investigations of the osmosis of the systems (7), (8) and (9), of which (8) was determined four times successively, it appears that the real D.T. always is the same as in (21).

So here the real- and the sluice D.T. would be identical only then, when the X- and W-curves of the bladder used, belonged to diagram I. Previously, however, we have seen that a bladder belongs to diagram I only in very special cases, namely when it had already passed through some absorption-periods (Chapter II Comm. I). As it is not probable now that the various bladders, used for the determination of the osmosis, should accidentally all have belonged to diagram I, we may assume that. at least in some of these cases, the real- and the sluice D.T. will be different.

In order to make this still more probable, we determined, as has also been indicated in table D:

1⁰. the absorption of a bladder successively in liquids, containing 0, 1.5 and 3 % of Na_2CO_3.

---

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

2) F. A. H. SCHREINEMAKERS and J. P. WERRE, Osmosis in systems, consisting of water and tartaric acid. These Proceedings **34**, pg. 42, 162 and 477 (1932).

2°. afterwards with this same bladder the osmosis in system (8) ; this determination was repeated a second time.

TABLE D.

		Sluice D. T.	Real D. T.
1°.	Absorption	$\leftarrow X \leftarrow o * W$	
2°.	Osmosis		$\leftarrow X \rightarrow W$
3°.	Absorption	$\leftarrow X \leftarrow o * W$	
4°.	Osmosis		$\leftarrow X \rightarrow W$
5°.	Absorption	$\leftarrow X \leftarrow o * W$	
6°.	Osmosis		$\leftarrow X \rightarrow W$

3°. afterwards with this same bladder again the absorption as in 1°.
4°. afterwards again with the same bladder the osmosis in system (8).
5°. afterwards again with this same bladder the absorption as in 1°.
6°. and at last again with this same bladder the osmosis in system (8).
From these determinations [1]) it appeared, as has been indicated also in table D, that the sluice D.T. of this system was always

$$\leftarrow X \quad \leftarrow o * W$$

and the real D.T. always:

$$\leftarrow X \quad \rightarrow W$$

From this we may conclude that the sluice D.T. and the real D.T. of this system are different.

From this it appears that in the systems (23), (24) and (25) the sluice D.T. and the real D.T. are identical, but that these two D.T.'s differ in (26).

Leiden, Lab. of Inorganic Chemistry.

[1]) C. L. DE VRIES, l.c. Table G and XXXII—XXXV.