genau angegebenen Verfahren und unter nicht genau beschriebenen Verhältnissen ermittelt wurden.

ZUSAMMENFASSUNG.

Es wurde nachgewiesen, dass Salizylsäurekristalle von etwa 0.01 mm Dicke (bei 25.00° C.) dieselbe Dichte aufweisen, wie solche deren entsprechende Dimension 1.0 mm beträgt. Innerhalb der Versuchsfehler ist $D^{4^\circ}_{25\,00^\circ} = \mathbf{1.4340}$.

VAN 'T HOFF-*Laboratorium.*

Utrecht, Okt. 1935.

Chemistry. — *An osmotic complex with two stationary liquids.* By F. A. H. SCHREINEMAKERS and J. P. WERRE.

(Communicated at the meeting of October 26, 1935).

§ 1. *Introduction* [1]).

First we take an osmotic complex.

$$inv.\ i_1 \,|\, L(z) \,|\, inv.\ i_2 \quad \ldots\ldots\ldots \quad (1)$$

with the invariant liquids i_1 and i_2 and one variable liquid z only. If we leave this complex alone, it will depend upon different factors whether it will pass into an osmotic equilibrium, a stationary or another state.

We now assume that the variable liquid z has a given constant pressure P_c and that it contains only substances, which may diffuse through both membranes. We shall represent the stationary state into which (1) then may pass, by

$$inv.\ i_1 \left| \begin{array}{c} m \times stat.\ L(s) \\ P_c \text{ given } \Delta m \lesseqgtr 0 \end{array} \right| inv.\ i_2 \quad \ldots\ldots \quad (2)$$
$$\longleftrightarrow \qquad\qquad \longleftrightarrow$$

in which the stat. liq. s has a definite composition, which does not change

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[1]) Comp. F. A. H. SCHREINEMAKERS, These Proceedings **34**, 78, 341, 524 and 823 (1931); **36**, 516, 717, 779 (1933).
F. A. H. SCHREINEMAKERS and J. P. WERRE, Rec. Trav. Chim. des Pays Bas **51**, 51, (1932),
J. P. WERRE, Dissertation, Leiden.
F. A. H. SCHREINEMAKERS and H. H. SCHREINEMACHERS, These Proceedings **35**, 1241 (1932); **36**, 629 (1933).

any more during the rest of the osmosis. The signs $\longleftrightarrow$ indicate that the osmosis is not over yet, but that each of the diffusing substances is still passing through both membranes; the diffusing quantities, however, have regulated themselves in such a way that the composition of liq. s does not change anymore. The quantity m of this liq. s, however, does change during the stat. osmosis; it may continuously increase or decrease, as has been indicated by $\triangle m \lesseqgtr 0$. (For examples compare l.c.)

The composition of this stat. liq. is determined by:

a. the composition and the pressure of the inv. liqs. i_1 and i_2.

b. the nature of the two membranes and the ratio of their surfaces.

c. the given constant pressure P_c.

When the var. liq. z of complex (1) does not yet contain all the diffusing substances of the liqs. i_1 and i_2, they will be absorbed during the transition to the stat. state. (For examples comp. l.c.)

When the variable liquid z contains other diffusing substances besides those occurring in i_1 and i_2, they will disappear during the transition to the stationary state (comp. § 3).

During the osmosis the variable liquid proceeds along a path, ending always in points s, no matter what composition this liquid z may have at the beginning of the osmosis. If e.g. this liquid should have respectively the compositions a, b, c etc., it will proceed along the paths as, bs, cs etc. resp. (For examples comp. l.c.)

§ 2. *There are two stationary liquids.*

We now take an osmotic complex

$$inv.\ i_1 \mid L\,(z) \mid L'\,(u) \mid inv.\ i_2 \quad \ldots\ldots\ldots \quad (3)$$

with the two variable liquids z and u; again we assume that they have respectively a constant pressure P_c and $P'_{c'}$, which may of course be the same or differ from each other; further we assume again that z and u contain only substances which may diffuse through the three membranes. We now can represent the stationary state by:

$$i_1 \left| \begin{array}{l} m \times stat.\ L\,(s) \\ P_c \text{ given } \triangle m \gtreqless 0 \end{array} \right| \begin{array}{l} m' \times stat.\ L'\,(s') \\ P'_{c'} \text{ given } \triangle m' \gtreqless 0 \end{array} \left| \, i_2 \right. \quad \ldots \quad (4)$$
$$\longleftrightarrow \qquad\qquad \longleftrightarrow \qquad\qquad \longleftrightarrow$$

in which each of the liquids s and s' will have a definite composition which does not change anymore during the rest of the osmosis. The signs $\longleftrightarrow$ also indicate here that each of the diffusing substances is still passing through each of the three membranes, so that the osmosis is going on all the time.

As has been indicated by $\triangle m \gtreqless 0$ and $\triangle m' \gtreqless 0$ the quantities m and m' of the stat. liquid do change during this stationary osmosis.

The composition of the stationary liquids s and s' is defined by the same factors a, b and c (§ 1); in b "both membranes" must now be replaced, however, by "the three membranes" and in c the two pressures P_c und $P'_{c'}$ are found. During the osmosis each of the variable liquids z and u will proceed along paths, ending respectively in the points s and s'. The composition, these liquids z and u may have at the beginning of the osmosis, is of no account here.

§ 3. *An osmotic complex of $NaCl + Na_2CO_3 + H_2O$ with two stationary liquids.*

In the osmotic complex

$$i_1\,(W)\,|\,L\,(z)\,|\,L'\,(u)\,|\,i_2\,(20.32\,\%\,NaCl) \quad . \; . \; . \; . \; . \quad (5)$$

with three membranes of pig's bladder the inv. liquid i_1 consisted of pure water and the inv. liq. i_2 had the composition

$$20.32\,\%\,NaCl + 79.68\,\%\,W.$$

During the osmosis the inv. and the var. liquids were under a pressure of one atmosphere.

When the liquids z and u contain other diffusing substances (e.g. Na_2CO_3) besides $NaCl + W$, they will be absorbed and carried away in the course of the osmosis by i_1 and i_2; (5) then passes into a stat. complex

$$\begin{array}{c|c|c|c} inv.\ i_1 & stat. & stat. & inv.\ i_2 \\ (water) & L\,(s) & L'\,(s') & (20.32\,\%\,NaCl) \end{array} \quad . \; . \; . \; . \; . \quad (6)$$

in which the stat. liquids s and s' contain $NaCl + W$ only.

1. At the beginning of the osmosis we gave the same composition to the liquids z and u, viz.

$$9.89\,\%\,NaCl + 7.09\,\%\,Na_2CO_3 + 83.02\,\%\,W \quad . \; . \; . \quad (7)$$

If we put $NaCl = X$ and $Na_2CO_3 = Y$ then we may imagine these liquids z and u represented by point a in the schematical fig. 1 and the liquids i_1 and i_2 by the points W and i_2.

It now appeared that during the osmosis liq. z proceeded along a path as and liq. u along a path as' (fig. 1).

We can draw these paths accurately with the aid of table 1. In column 1 we find the number of the determinations, in column 2 the time in days,

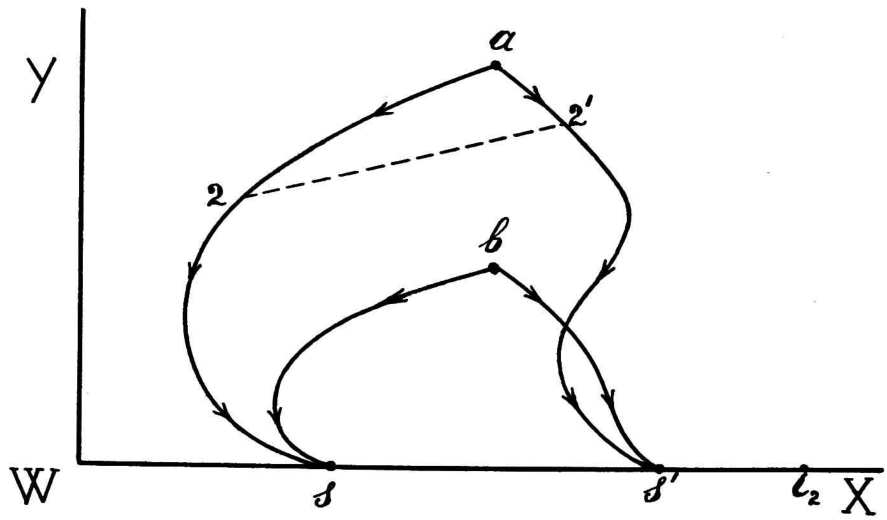

Fig. 1

passed after the beginning of the osmosis; in columns 3 and 4 we find the composition of the variable liquid z and in 5 and 6 the composition of the variable liquid u.

It appears from this table that after 36 days z and u had got respectively the compositions,

$$6.38\ \%\ NaCl + 0.05\ \%\ Na_2\,CO_3 + 93.57\ \%\ W \quad . \quad . \quad . \quad (8)$$

$$13.37\ \%\ NaCl + 0.09\ \%\ Na_2\,CO_3 + 86.54\ \%\ W \quad . \quad . \quad . \quad (9)$$

As the two liquids had been changing their compositions only very slowly during the last 10 days and as the Na_2CO_3 had almost disappeared already, we may assume that the liquids z and u have almost reached the stationary points s and s'.

It appears from table 1 and the shape of the paths as and as' that during the osmosis the $NaCl$-amount of liquid z passes through a minimum and that of liquid u first through a maximum and afterwards through a minimum.

If we call 2 liquids, present in an osmotic complex at the same moment, conjugated liquids, then a definite liquid of path as' is conjugated with each liquid of path as and reversally; e.g. liq. 2 with 2′ (viz. N⁰. 2 of table 1). As it appears from table 1 that liq. z always has a smaller Na_2CO_3-amount than liq. u, all conjugation-lines will incline towards the left. (comp. 2, 2′)

TABLE 1

No.	t in days	Comp. of $L(z)$		Comp. of $L(u)$	
		% Na Cl	% $Na_2 CO_3$	% Na Cl	% $Na_2 CO_3$
1		9.89	7.09	9.89	7.09
2	2	5.58	5.00	10.99	5.99
3	4	4.24	3.55	11.74	4.65
4	6	3.93	2.31	11.99	3.54
5	8	4.28	1.64	11.21	2.83
6	10	4.39	1.23	10.92	2.26
7	12	4.68	0.95	11.06	1.72
8	16	5.33	0.54	12.05	0.94
9	20	5.96	0.31	12.70	0.50
10	26	6.18	0.13	13.09	0.20
11	36	6.38	0.05	13.37	0.09

2. For a new series of determinations the composition

$$9.92\,\%\, NaCl + 4.16\,\%\, Na_2\,CO_3 + 85.92\,\%\, W \ldots \quad (10)$$

was given to the two liquids z and u at the beginning of the osmosis; in fig. 1 this is represented by point b. It now appeared that during the osmosis liquid z proceeded along path bs and liquid u along path bs'; these paths can be drawn accurately with the aid of table 2, arranged in the same way as table 1.

It appears from the table that after 27 days the liquids z and u had obtained respectively the compositions

$$6.84\,\%\, NaCl + 0.02\,\%\, Na_2\,CO_3 + 93.14\,\%\, W \ldots \quad (11)$$

$$14.05\,\%\, NaCl + 0.03\,\%\, Na_2\,CO_3 + 85.92\,\%\, W \ldots \quad (12)$$

It appears from table 2 and the shape of the paths bs and bs' that the $NaCl$-amount of liquid z once more passes through a minimum during the osmosis; path bs', however, followed by liquid u, shows neither a maximum nor a minimum any more, but does show a point of inflection.

3. It appears from (8), (9), (11) and (12) and the determinations (14) and (15) to be discussed later on, that the stationary liquids s and s'

TABLE 2

No.	t in days	Comp. of $L(z)$		Comp. of $L(u)$	
		% NaCl	% Na_2CO_3	% NaCl	% Na_2CO_3
1		9.92	4.16	9.92	4.16
2	2	5.67	2.55	12.18	2.99
3	4	5.12	1.63	12.47	2.13
4	6	5.33	1.09	12.65	1.50
5	10	5.94	0.53	12.97	0.75
6	16	6.28	0.19	13.50	0.27
7	27	6.84	0.01	14.05	0.03

contain approximately ± 7 % and ± 14.1 % of *NaCl* and of course no Na_2CO_3. We now represent this stat. state by:

$$\begin{array}{c|c|c|c} inv.\ i_1 & m \times stat.\ (7) & m' \times stat.\ (14{,}1) & inv.\ i_2 \\ (W) & \triangle m < 0 & \triangle m' > 0 & (20.32) \\ \multicolumn{2}{c}{\rightarrow W} & \rightarrow W & \rightarrow W \\ \multicolumn{2}{c}{\leftarrow NaCl} & \leftarrow NaCl & \leftarrow NaCl \end{array} \quad . \; . \quad (13)$$

in which the numbers indicate the procents of *NaCl*. It appears from the determinations that the quantity of the left stat. liquid decreased ($\triangle m < 0$) and that of the right liquid increased ($\triangle m' > 0$). Through each of the three membranes a *W*-current flows and a *NaCl*-current; if we pay attention to $\triangle m < 0$ and $\triangle m' > 0$, it appears that the strongest water-current and the weakest *NaCl*-current pass through the central membrane.

4. When a complex contains one variable liquid only, this liquid will, during the transition towards the stationary state proceed along a path, the shape of which does not depend on the quantity of the liquid; this quantity namely influences only the velocity with which the liquid proceeds along that path.

In a complex with 2 (or more) variable liquids the shape of the path does depend upon the quantity of each of the var. liquids. In a complex with one var. liq. only it is situated between the inv. liquids i_1 and i_2; in complex (3) z is situated between i_1 and u, and u is situated between z and i_2.

As z is situated between i_1 and u, the change of z therefore will depend at any time upon the composition of u, which changes at a quicker or a slower rate, in accordance with the quantity being smaller or greater. The same rate obtains for liquid u, situated between z and i_2. From the above follows that the shape of the paths of liqs. z and u will depend on the quantities of this liquid. The final state of the complex (viz. the composition of the stat. liquids s and s', the direction in which the substances pass through the membranes during the osmosis, etc.) does not depend on these quantities of course.

In order to prove this, the paths starting from point a (fig. 1) were determined once more, but with other quantities of the liquids z and u. It appears from table 3 that the liquids z and u had after 29 days got resp. the compositions:

$$6.54\ \%\ NaCl + 0.03\ \%\ Na_2\,CO_3 + 93.43\ \%\ W \quad . \quad . \quad . \quad (14)$$

$$13.69\ \%\ NaCl + 0.06\ \%\ Na_2\,CO_3 + 86.25\ \%\ W \quad . \quad . \quad . \quad (15)$$

If we draw these paths in fig. 1 with the aid of table 3, we see that they are situated quite differently from the paths drawn already.

TABLE 3

No.	t in days	Comp. of $L(z)$		Comp. of $L(u)$	
		% Na Cl	% Na_2CO_3	% Na Cl	% Na_2CO_3
1		9.87	7.09	9.87	7.09
2	2	5.14	4.10	11.33	5.00
3	4	4.37	2.60	11.69	3.63
4	6	4.44	1.75	11.98	2.63
5	8	4.77	1.21	11.74	1.91
6	10	5.01	0.84	12.17	1.33
7	14	5.62	0.43	12.65	0.65
8	20	6.05	0.15	13.20	0.23
9	29	6.54	0.03	13.69	0.06

We then see that the $NaCl$-amount of liquid z once more passes through a minimum indeed, but that this new path as is situated entirely within the concave side of the first. The $NaCl$-amount of liquid u passes through a maximum and minimum indeed which are only faintly marked however; the new path as' intersects the first in a point between the maximum and minimum.

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