a. $P_e > P_i$. Now a system forms:

$$\times_{Pe} \mid inv.\, L_i\, (d + X + Z)_{Pi} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

b. $P_e < P_i$. Now a system forms:

$$\uparrow_{Pe} \mid inv.\, L_i\, (d + X + Z)_{Pi} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

From these examples it appears that the becoming more- or m.l.-permeable can cause all sort of changes in the e-state; in some cases the quantity of liquid e even can increase continuously (19, 22 and 25); in other cases liquid e can completely disappear (18 and 24). The latter case, as is evident without adding anything, is possible only when the membrane becomes permeable for all substances of liquid e.

Corresponding considerations obtain also when the liquid e has been shut up in a space with constant volume; then we have a onesided Def. V.Q.-equilibrium. As, however, the pressure in this space will regulate itself, it is clear that the cases 18, 19, 22, 24 and 25 discussed above, cannot occur then. A closer examination of these cases is left to the reader.

Instead of a liquid e we can also imagine that a tissue e is in osmotic equilibrium with a liquid i, flowing past it; that tissue can be under constant pressure, or it can be shut up in a non-elastic or in an elastic film. Every change in the membrane causing it to become more or m.l. permeable, will cause corresponding changes of state as have been described above.

A consideration of the case that successive changes in the permeability occur, is left to the reader (comp. also Comm. II).

(To be continued.)

Leiden, Lab. of Inorg. Chemistry.

Chemistry. — *Osmosis in systems consisting of water and tartaric acid and containing three liquids, separated by two membranes.* I. By F. A. H. SCHREINEMAKERS and H. H. SCHREINEMACHERS.

(Communicated at the meeting of December 17, 1932).

I.   *Introduction.*

We take an osmotic system

$$L_1 \mid L \mid L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

containing three liquids and two membranes. If we leave this system alone, the three liquids will change their compositions until an equilibrium arises towards the end of the osmosis. When the two membranes are permeable for all substances, then towards the end of the osmosis an equilibrium

$$L_e \mid L_e \mid L_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will arise, in which all liquids have the same composition e. This composition e depends upon the composition and the ratio of the quantities of the three liquids in system (1).

When the liquids of system (1) contain the substances W, X and Y, each of these liquids will proceed along a path in the WXY-diagram; at the end of the osmosis these three paths will end in the same point e.

In the systems

$$\text{water} + \text{NaCl} + \text{Na}_2\text{CO}_3$$
$$\text{and water} + \text{NH}_4\text{Cl} + \text{NH}_4\text{-succinate}$$
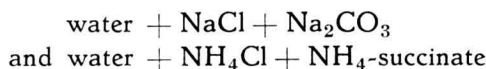
several of these paths have been determined experimentally by F. A. H. SCHREINEMAKERS, L. J. VAN DER WOLK and G. BERKHOFF [1]).

If we now assume that the compositions of the liquids L_1 and L_2 of system (1) are kept invariant during the entire osmosis (or during the time in which we examine the osmosis) then we shall represent it by

$$inv. \, L\,(i_1) \overset{M_1}{\underset{\omega_1}{|}} L\,(z) \overset{M_2}{\underset{\omega_2}{|}} inv. \, L\,(i_2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which M_1 and M_2 represent the two membranes and ω_1 and ω_2 their surfaces.

When the osmosis begins in this system, so that the substances may pass through the two membranes with various velocities and in various directions, then liquid $L(z)$ will change its composition; it will not become equal, however, to $L(i_1)$ nor to $L(i_2)$ and nor will an equilibrium occur, but a stationary state will set in, which we shall represent by

$$inv. \, L\,(i_1) \overset{M_1}{\underset{\omega_1}{|}} stat. \, L\,(s) \overset{M_2}{\underset{\omega_2}{|}} inv. \, L\,(i_2) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The composition of this stationary liquid $L(s)$ depends upon [2]) ·
1. the composition of the two invariant liquids i_1 and i_2;
2. the nature of the membranes M_1 and M_2;
3. the ratio of their surfaces ω_1 and ω_2.

Every change in one of these factors will, therefore, also cause a change of the stationary liquid s.

We have said above that (4) is not an equilibrium, but a stationary state; the osmosis namely is not yet over then, for as the three liquids still have different compositions, the substances will still go on diffusing continuously in some direction through both membranes; these diffusing quantities, however, have now regulated themselves in such a way, that the composition of liquid s does not change any more; in general the quantity of this liquid s goes on changing all the time and may increase as well as decrease.

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[1]) Comp. G. BERKHOFF, Dissertation, Leiden 1929.

[2]) F. A. H. SCHREINEMAKERS, These Proceedings 34, 78. 341, 524 and 823 (1931).

The composition of the stationary liquid s of system (4) is of course independent of the composition, the variable liquid z of system (3) has at the beginning of the osmosis.

When at the beginning of the osmosis liquid z has e.g. the composition a, then during the osmosis the variable liquid will proceed along a path as, which begins in a and ends in s; when at the beginning of the osmosis liquid z has e.g. the composition b, then during the osmosis the variable liquid proceeds along a path bs, etc.

Consequently an ∞ number of paths exists, along which a variable liquid may travel; these paths, which all end in point s, form the bundle[3]) of point s.

In the osmotic system

$$inv. \, (Water) \mid L \, (z) \mid inv. \, L \, (i_2). \qquad . \quad . \quad . \quad . \quad . \quad (5)$$
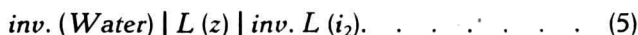
in which the invariant liquid i_2 contained the substances

$$Water + NaCl + Na_2CO_3$$

the composition the stationary liquid s gets, several paths of a variable liquid, the influence of the nature of the membranes, etc. have been determined experimentally[4]).

In order to make it easier to grasp the phenomena, which may occur with the osmosis in systems, consisting of water and tartaric acid and containing three liquids, it is advisable to become acquainted with the osmosis in the simpler case that there are only two liquids. Although this osmosis has already been described previously[5]) for several of these systems, we shall yet briefly consider one of these systems, which it is absolutely necessary to know; this is the system:

$$inv. \, (Water) \mid L \, (W + Tartaric \; acid) \quad . \quad . \quad . \quad . \quad (6)$$

in which on the left side of the membrane pure water, which during the entire osmosis being refreshed continuously and hence kept practically invariant. If the membrane is permeable for both substances, then it is clear that during the entire osmosis the tartaric acid will diffuse $\leftarrow$, namely from the solution towards the pure water. We now consider two membranes.

1. The membrane consists of cellophane. The experiment taught us, that during the entire osmosis the substances diffused according to the D.T.

$$\rightarrow W \qquad \leftarrow Tartaric \; acid \, . \quad . \quad . \quad . \quad . \quad (7)$$

no matter what concentration the variable liquid L might have.

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[3]) For the properties of the paths of this bundle comp. note 2.

[4]) F. A. H. SCHREINEMAKERS and J. P. WERRE. Rec. des Trav. Chim. des Pays Bas **51** 51 (1932).

    J. P. WERRE. Dissertation. Leiden 1931.

    L. J. v. D. WOLK. Dissertation. Leiden 1932.

[5]) F. A. H. SCHREINEMAKERS and J. P. WERRE. These Proceedings **35** 42, 162 and 477 (1932).

    J. P. WERRE. Dissertation. Leiden 1931.

So, during the osmosis the water flows from the pure water towards the solution.

2. The membrane consists of a pig's bladder. Now the experiment taught us that the direction of diffusion of the water depends upon the concentration of the variable liquid and that no water will diffuse, when this liquid contains a definite amount of tartaric acid; for the sake of simplicity we shall call this liquid the neutral liquid of this system and we represent it by L_n.

When the variable liquid now contains a smaller amount of tartaric acid than the neutral liquid L_n, then during the entire osmosis the substances will diffuse according to (8), namely according to the D.T.

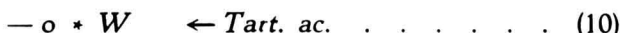$$\leftarrow o \ast W \qquad \leftarrow Tart.\ ac. \ . \ . \ . \ . \ . \ . \quad (8)$$
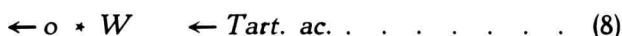
Then, namely during the entire osmosis the water flows from the solution towards the pure water and consequently, as has been indicated also by the signs o and $\ast$, incongruently and negatively.

If, however, at the beginning of the osmosis the variable liquid contains a greater amount of tart. ac. than liquid L_n, the substances will run through the membrane first according to the D.T.

$$\rightarrow W \qquad \leftarrow Tart.\ ac. . \ . \ . \ . \ . \ . \ . \quad (9)$$

which is the same as (7).

As during the osmosis the amount of tart. ac. of the variable liquid decreases, however, a moment is coming at which this liquid will get the same composition as the neutral liquid L_n; as then no water flows through the membrane, at this moment we have the D.T.

$$- o \ast W \qquad \leftarrow Tart.\ ac. \ . \ . \ . \ . \ . \quad (10)$$

This D.T., however, exists only a single moment, for, as the tart. acid always diffuses towards the left, the variable liquid now gets a smaller amount of tart. ac. than liquid L_n. Then the substances diffuse according to (8) viz. according to the D.T.

$$\leftarrow o \ast W \qquad \leftarrow Tart.\ ac. \ . \ . \ . \ . \ . \quad (11)$$
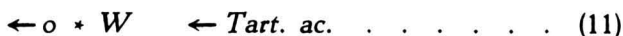
From this it appears that the direction in which the water will diffuse during the osmosis through a pig's bladder, depends upon the concentration of the variable liquid at the beginning of the osmosis.

If this concentration is smaller than that of the neutral liquid, then during the entire osmosis the water will diffuse $\leftarrow o \ast$ namely from the solution towards the pure water.

If this concentration is greater than that of the neutral liquid then the water will first diffuse $\rightarrow$ and afterwards $\leftarrow o \ast$, viz. first towards the solution and afterwards until the end of the osmosis from the solution towards the pure water.

It appeared from the experiment, as was indeed to be expected, that the composition of this neutral liquid L_n depends upon the nature of the pig's bladder used; with one of these bladders we found $\pm$ 14 %, with an other $\pm$ 17 % and with a third $\pm$ 21 % of tart. acid.

II. The osmotic system

$$inv. \ (W) \overset{bl.}{\vert} L\ (z) \overset{bl.}{\vert} inv. \ L' \ (14.35 \ ^0/_0 \ tart. \ ac.) \ . \ . \ . \ . \ (12)$$

The left side invariant liquid of this system consists of pure water, the right-side of a solution, containing 14.35 % of tart. ac.; the two membranes consist of a pig's bladder.

Now, no matter what composition it has at the beginning of the osmosis. the liquid z must pass into a stationary liquid s; it appeared from the experimental determinations that it contained $\pm$ 7.423 % of tart. ac. We now represent the stationary state of system (12) by

$$inv. \ (W) \overset{bl.}{\vert} stat. \ (\pm \ 7.423 \ ^0/_0) \overset{bl.}{\vert} inv. \ L' \ (14.35 \ ^0/_0 \ tart. \ ac.) \ . \ . \ (13)$$

In order to find this stationary state we took in (12) for $L(z)$ pure water at the beginning of the osmosis; consequently we started from the system

$$inv. \ (W) \overset{bl.}{\vert} L \ (beg. \ Water) \overset{bl.}{\vert} inv. \ L' \ (14.35 \ ^0/_0 \ tart. \ ac.) \ . \ . \ (14)$$

and we found that it had passed into the stationary state (13) after 820 hours.

The data for this osmosis are found in table 1. In the first column we

TABLE 1.

N⁰.	t in hours	$^0/_0$ tart. ac. of the variable liq.	Diffused to the variable liq.		$\Delta\ m$
			gr. tart. ac.	gr. W	
1	0	0			
2	24	1.636	+ 7.902	− 3.898	+ 4.004
3	67	3.686	+ 9.443	− 10.318	− 0.875
4	139	5.787	+ 8.910	− 16.190	− 7.280
5	139	5.424			
6	235	6.543	+ 4.420	− 25.778	− 21.358
7	396	7.209	+ 0.700	− 36.003	− 35.303
8	567	7.385	− 1.930	− 34.727	− 36.657
9	734	7.465	− 2.920	− 40.340	− 43.260
10	820	7.423	− 1.910	− 21.845	− 23.755

find the number of the successive determinations, in the second column the number of hours that passed after the beginning of the osmosis; in the third column we find the amount of tart. ac. of the variable liquid. In the fourth and fifth columns we find the number of grams of tart. ac. and water, which have been taken in (sign +) or given off (sign —) by the variable liquid between two successive determinations. From these two columns the last column follows at once, namely the total quantity of $\triangle m$ taken in (sign +) or given off (sign —) by the variable liquid.

This table contains two series of determinations namely Nos. 1—4 and Nos. 5—10. From Nos. 1—4 appears that the amount of tart. acid of the variable liquid had increased after 139 hours from 0 to 5.787 %. As too little of this liquid then remained for other determinations, it was replaced by a new one (namely No. 5 with 5.424 %) with which the determinations Nos. 5—10 were made.

We see that the amount of tart. ac. increases only very slowly starting from No. 7 and that in 10 it even becomes somewhat lower than in 9. This indicates that the variable liquid has approached its stationary composition; if we take the factors into consideration, determining this composition (comp. the introduction) it is clear that it will continuously show small changes; for this reason $\pm$ 7.423 % has been assumed in (13).

From column 4 it appears that during the osmosis the variable liquid first takes in tart. ac. (Nos. 1—7) and afterwards gives it off again; from column 5 it appears that during the entire osmosis this liquid gives off water; from column 6 it appears that the quantity of this liquid increases only at the beginning of the osmosis and afterwards decreases continuously.

For an other series of determinations we took in (12) for $L(z)$ a solution of 40.15 % tart. ac. at the beginning of the osmosis; so we now started from the system

$$inv. \ (W) \overset{bl.}{|} L \ (beg. \ 40.15 \ ^0/_0) \overset{bl.}{|} inv. \ L' \ (14.35 \ ^0/_0) \quad . \quad . \quad . \quad (15)$$

The data for the osmosis in this system are found in table 2, which has been arranged in the same way as table 1; when taking count of the numbers, attention should be paid to the fact that this table contains four series of determinations.

We see that the amount of tart. ac. of the variable liquid now decreases continuously; between Nos. 8 and 9 this liquid gets the same composition as the invariant liquid (14.35 %), after which it decreases to 8.416 %. If circumstances had not prevented our making further determinations, we should have seen this amount of tart. ac. decreasing until about $\pm$ 7.423 %. That the variable liquid had not yet reached its stationary composition here, also appears from the still relatively rapid decrease of its amount of tart. ac. (comp. the very slow increase in table 1).

From columns 4 and 5 it appears that during the entire osmosis the

TABLE 2.

N⁰.	t in hours	% tart. ac. of the variable liq.	Diffused to the variable liq.		Δ m
			gr. tart. ac.	gr. W	
1	0	40.15			
2	18	35.80	− 20.05	+ 26.677	+ 6.627
3	18	34.43			
4	42	29.93	− 21.61	+ 21.255	− 0.355
5	90	22.84	− 36.04	+ 25.771	− 10.269
6	90	28.24			
7	163	20.22	− 44.40	+ 32.870	− 11.53
8	227	15.60	− 26.03	+ 9.648	− 16.382
9	350	10.91	− 25.70	− 1.124	− 26.824
10	350	13.59			
11	469	9.763	− 19.766	− 9.113	− 28.879
12	597	8.416	− 7.860	− 20.740	− 28.600

variable liquid gives off tart. ac. and that in the first part of the osmosis it takes in water, giving it off afterwards; from column 6 it appears that the quantity of this liquid first increases and afterwards decreases.

In the introduction we have seen that after the setting in of the stationary state, the osmosis generally continues all the time. Now it appears from the columns 4—6 of tables 1 and 2 that there is still a strong osmosis, even when the variable liquid has come in the vicinity of its stationary composition; this obtains for concentrations smaller (table 1) as well as greater (table 2) than the one of the stationary composition. As the variable liquid continuously gives off tart. ac. and water here and as its quantity continuously decreases, we now represent (13) by

$$\text{inv. } (W) \quad \left|\begin{array}{c} \overset{bl.}{} \\ \text{stat. } (\pm\, 7.423) \\ \text{tart. ac. } -; \; W- \end{array}\right|^{\overset{\triangle m-}{}} \quad \overset{bl.}{} \text{inv. } L' \,(14.35). \quad . \quad . \quad (16)$$

in which it has been indicated that the stationary liquid continuously gives off tart. acid and water and that its quantity decreases continuously.

Now we must still find out in what directions the two substances pass through each of the two membranes. From the determinations in systems with only a single membrane (comp. introduction and note 5) it is obvious
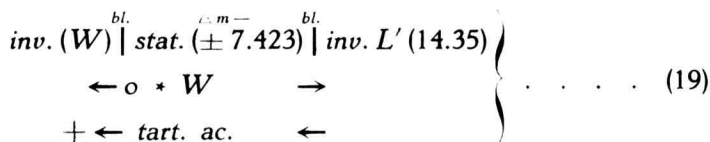
that through the left-side bladder the osmosis will take place according to the D.T.

$$\leftarrow o * W \qquad \leftarrow Tart.\ ac. \quad . \quad . \quad . \quad . \quad . \quad (17)$$
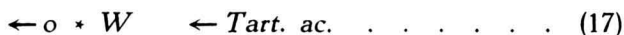
and through the right-side bladder according to the D.T.

$$\rightarrow W \qquad \leftarrow Tart.\ ac. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

We now represent (16) by

$$
\begin{array}{l}
inv.\ (W) \overset{bl.}{|} stat.\ \overset{\triangle m -}{(\pm 7.423)} \overset{bl.}{|} inv.\ L'\ (14.35) \\
\quad \leftarrow o * W \qquad \rightarrow \\
+ \leftarrow\ tart.\ ac. \qquad \leftarrow
\end{array} \quad . \quad . \quad . \quad (19)
$$

which shows that water diffuses away towards the left and towards the right, whereas tart. ac. flows inwards through the right-side membrane and outwards through the left-side membrane. As, however, the composition of the stationary liquid does not change, a quantity of tart. ac. will have to diffuse away greater than the quantity that will diffuse inwards through the right-side membrane; this has been indicated by the sign + with the corresponding arrow.

In order to examine also this, we took the system

$$L_1\ (Water) \overset{bl.}{|} L\ (7.423) \overset{bl.}{|} L'\ (14.34). \quad . \quad . \quad . \quad . \quad (20)$$
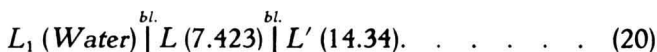
in which we have to take the three liquids variable now, to enable us to make our determinations.

After 43 hours the left-side liquid contained 1.706 %, the middle-liquid 7.512 % and the right-side liquid 13.03 % of tart. acid. Further it appeared that 5.114 gr. of water had diffused ← o * and 1.690 gr. of water → and that 6.191 gr. of tart. ac. had diffused through the left-side membrane ← and 5.78 gr. of tart. ac. through the right-side membrane also ←. So in (20) more tart. ac. had indeed diffused away through the left-side membrane than inwards through the right-side membrane.

III. The osmotic system

$$inv.\ (W) \overset{cell.}{|} L\ (z) \overset{bl.}{|} inv.\ L'\ (3.999\ ^0/_0\ tart.\ ac.) \quad . \quad . \quad . \quad (21)$$
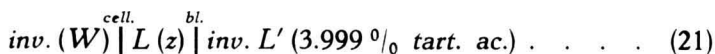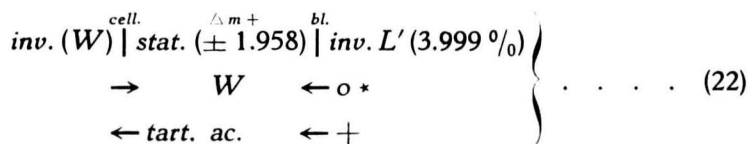
The right-side liquid of this system contained 3.999 % of tart. ac.; the left-side membrane consisted of cellophane, the right-side membrane of a pig's bladder.

At the beginning of the osmosis we took a solution with 1.912 % of tart. ac. After 164, 331 and 475 hours the variable liquid contained resp. 2.02 %, 1.98 % and 1.958 % of tart. acid. This slow change indicates that the variable liquid was in the vicinity of its stationary composition. The volume of this liquid went on increasing during the entire osmosis.

From the determinations in systems with only one membrane follows that we now can represent the osmosis by the arrows in

$$inv.\,(W) \overset{cell.}{|}\, stat.\,(\pm\, \overset{\triangle m+}{1.958}) \overset{bl.}{|}\, inv.\,L'\,(3.999\,\%)$$
$$\rightarrow \qquad W \qquad \leftarrow o\star$$
$$\leftarrow tart.\,ac. \qquad \leftarrow + \qquad\qquad\qquad (22)$$

so that the water-movement is now quite different from that in (19). Now we see also, as has been indicated by the sign $+$ with an arrow, that more tart. ac. must diffuse through the bladder than through the cellophane.

Then we took the osmotic system

$$L_1\,(W) \overset{cell.}{|}\, L\,(1.958) \overset{bl.}{|}\, L'\,(3.999\,\%) \qquad\qquad (23)$$

in which the three liquids were variable now. After 42 hours the left-side liquid contained 0.391 %, the middle liquid 1.937 % and the right-side liquid 3.609 % of tart. acid. We found that at the time 6.097 gr. of water had diffused $\rightarrow$ and 1.536 gr. of water $\leftarrow o\star$ and that 1.499 gr. of tart. ac. had passed through the bladder and 1.380 gr. of tart. ac. through the cellophane.

IV.   The osmotic system

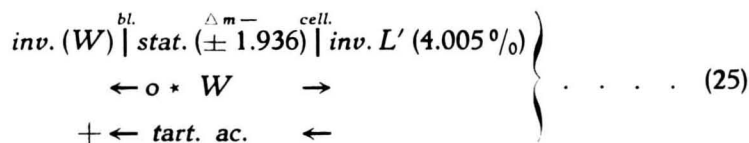$$inv.\,(W) \overset{bl.}{|}\, L\,(z) \overset{cell.}{|}\, inv.\,L'\,(4.005\,\%\,\, tart.\,ac.) \qquad\qquad (24)$$
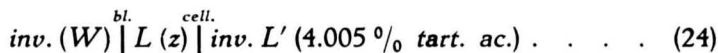
The right-side liquid of this system practically has the same composition as in (21). Yet, as will appear later on, the osmosis proceeds quite differently as it did in (22), because the two membranes have been changed now.

At the beginning of the osmosis we now took for $L(z)$ a solution with 1.937 % of tart. ac. After 143 and 236 hours the variable liquid contained 1.910 % and 1.936 % of tart. ac. so that the variable liquid was in the vicinity of its stationary composition. The volume of this liquid went on decreasing continuously.

From the determinations in systems with one membrane follows that we now can represent the osmosis by the arrows in

$$inv.\,(W) \overset{bl.}{|}\, stat.\,(\pm\, \overset{\triangle m-}{1.936}) \overset{cell.}{|}\, inv.\,L'\,(4.005\,\%)$$
$$\leftarrow o\star \quad W \qquad \rightarrow$$
$$+ \leftarrow tart.\,ac. \qquad \leftarrow \qquad\qquad\qquad (25)$$

so that the change of the quantity and the water-movement are now quite otherwise than in (22). The sign $+$ with an arrow indicates that now more tart. ac. must diffuse through the bladder than through the cellophane.

Then we took the osmotic system

$$L_1\,(W) \overset{bl.}{|}\, L\,(1.936) \overset{cell.}{|}\, L'\,(4.005\,\%) \qquad\qquad (26)$$

in which the three liquids were variable. After 46 hours the left-side liquid

contained 0.449 %, the middle-liquid 1.952 % and the right-side liquid 3.498 % of tart. ac. We found that then 4.426 gr. of water had diffused ← o⋆ and 5.421 gr. of water → and that 1.759 gr. of tart. ac. had diffused through the bladder and 1.624 gr. of tart. ac. through the cellophane.

The systems (22) and (25) have practically the same invariant liquids, the membranes, however, have been changed; as is apparent from the arrows and the sign of $\triangle m$, this has a great influence on the osmosis; this was indeed to be expected as also appears from the introduction. In (22) the water diffuses inwards through both membranes and the quantity of the stationary liquid increases continuously; in (25) the water diffuses outwards through both membranes and the quantity of the stationary liquid decreases continuously.

(To be continued.)

Leiden. Lab. of Inorg. Chemistry.

Chemistry. — *The Formation of Cyclic Compounds of Pyrocatechol with Aldehydes and Ketones.* By Prof. J. BÖESEKEN and G. SLOOFF.

(Communicated at the meeting of December 17, 1932).

In aliphatic chemistry we know many condensation products between diols (1.2 as well as 1.3) and aldehydes and ketones, compounds which may be represented thus:
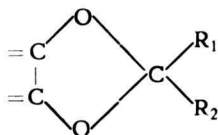
Likewise similar compounds have been separated (especially with acetone) with the hydromates. Of the aromates only pyrocatechol and derivatives deserve consideration as regards formation of such compounds. So far only the condensation product with formaldehyde, pyrocatechine methylene ether was known. This compound was first prepared by MOUREU [1], not by condensation of pyrocatechol with formaldehyde itself, but through treatment of the sodium salt of pyrocatechol with methylene iodide. Later also the cheaper methylene chloride was used. The amount yielded is not given, but it is very small. There exists a good deal of literature on the derivatives, among which safrole, piperonal, myristicine, and apiole. In the study of these derivatives the natural products or products derived from them (piperonal) are always taken as starting point.

Efforts to condense pyrocatechol with aldehydes or ketones have certainly not been wanting, the more so as acetone is largely used for the deter-

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[1] MOUREU. Bull. Soc. Chim. **15**. 654.