This is not possible from the mutual densities of the parabolas 2, 3, or 4. because these are owing to two different kinds if ions[1]).

A serious objection to a determination of the mixing proportion of the isotopes lies, however, in the fact that this cannot be considered as constant during the exposition. Probably in consequence of cleaning up by the aluminium electrodes, at first relatively more H^2 than H^1 atoms are withdrawn from the gasfilling. Possibly a state of equilibrium is only gradually established.

When once a density curve shall have been obtained, the variation of the concentration with the time can be quantitatively found by taking a series of short timed photos, and the different circumstances which are of influence here can be examined.

---

[1]) On the Plate the ions between square brackets always are the combinations with the smaller probability. The parabolas of both kinds of ions always coincide, because their mass difference is too small for obtaining separation. We have succeeded however by taking photographs of a mixture of He and concentrated hydrogen, to separate the hydrogen ions with masses 4,5 and 6 from He^+, HeH^{1+}, HeH^{2+}. In a following communication we intend to give details of this method of exhibiting the mass defect.

Chemistry. — *Stationary, checked and other states of osmotic systems.* II.

By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of September 30, 1933).

Stationary states in osmotic systems in which several substances can diffuse.

In the preceding communication we have discussed a few stational states of osmotic systems with membranes permeable for one substance only, viz. water; now we shall consider the case that more substances may diffuse. For this purpose we take the osmotic system

$$inv\ i_1 \mid L \mid inv\ i_2 \quad \ldots \ldots \ldots \quad (1)$$

in which we take the substances and concentrations of the three liquids and the permeability of the two membranes quite arbitrarily. If we leave this system alone, the variable liquid L will go on changing its composition until at a certain moment of the osmosis, as we shall see further on, a stational state

$$inv\ i_1 \mid stat\ L \mid inv\ i_2 \quad \ldots \ldots \ldots \quad (2)$$

will occur, in which liquid L does not change its composition any longer.

Of course all the diffusing substances of the liquids i_1 and i_2 will be present in the stationary liquid of (2), no matter whether these substances were or were not present already in the variable liquid of (1). Diffusing substances of liquid L in (1), which are not present in i_1 and i_2, will be taken in and removed from the system by the invariant liquids during the osmosis, so that they are no longer present in (2).

When the variable liquid L of (1) also contains non-diffusing substances, then of course they will still be found in the stat. liquid of (2); of course these non-diffusing substances may be the same as those of the liquids i_1 and i_2, but they may also be different; besides it is possible that either of these liquids i_1 and i_2 or both do not contain non-diffusing substances.

We now represent this stationary state by:

$$inv\ i_1 \overset{M_1}{|}\ stat\ L\,(d+d_1+d_2+n) \overset{M_2}{|}\ inv\ i_2\,.\ \ .\ \ .\ \ .\ \ .\quad (3)$$

in which we have indicated that the stat. liquid contains:

d diffusing substances, which may pass through each of the two membranes.

d_1 diffusing substances, which may pass only through the membrane M_1.

d_2 diffusing substances, which may pass only through the membrane M_2.

n non-diffusing substances.

First we are now going to consider some special cases of (3).

A. If we put $d_1=0$ $d_2=0$ and $n=0$, we get

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

in which each of the d substances present may pass through both membranes. If, for the sake of concentration we take the three substances Water, X and Y, we may represent (4) by

$$inv\ i_1 \underset{\omega_1}{\overset{M_1}{|}}\ stat\ L\,(W+X+Y) \underset{\omega_2}{\overset{M_2}{|}}\ inv\ i_2\ \ .\ \ .\ \ .\ \ .\ \ .\quad (5)$$

The quantity of water, diffusing per sec. through 1 cM^2 of the membrane M_1 depends upon the composition of the liquids i_1 and L and on their pressures P_1 and P. We represent this quantity by $\varphi_{1.w}(i_1\ L\ P_1\ P)$ which function of course besides contains the magnitudes determining the nature of the membrane M_1; the indices 1 and w indicate that this function obtains for the membrane M_1 and the substance W. If we represent the quantities of X and Y, diffusing per sec. through 1 cM^2 of the membrane M_1 in a similar way, we have the 3 M-functions

$$\varphi_{1.w}(i_1\,L\,P_1\,P)\quad,\quad \varphi_{1.x}(i_1\,L\,P_1\,P)\quad \text{and}\quad \varphi_{1.y}(i_1\,L\,P_1\,P)\ \ .\ \ .\quad (6)$$

which we shall call membranes- or M-functions.

For the quantities of W, X and Y diffusing per sec. through 1 cM^2 of the membrane M_2 we have the three M-functions:

$$\varphi_{2.w}(i_2\,L\,P_2\,P)\quad,\quad \varphi_{2.x}(i_2\,L\,P_2\,P)\quad \text{and}\quad \varphi_{2.y}(i_2\,L\,P_2\,P)\ \ .\ \ .\quad (7)$$

which besides contain the magnitudes, determining the nature of the membrane M_2.

As we can represent the composition of liq. L by

$$x\,gr\,X + y\,gr\,Y + (1-x-y)\,gr\,W\ \ .\ \ .\ \ .\ \ .\ \ .\quad (8)$$

this will contain the 2 variables x and y; so each of the M-functions contains the 3 variables x, y and P.

For the sake of concentration we now shall assume that the sign of an M-function has been chosen in such a way that it is positive when the substance is taken in by liq. L and negative when it is given off by liq. L. The quantities of X, Y and W taken in per sec. by liq. L then are:

$$\omega_1\, \varphi_{1.x} + \omega_2\, \varphi_{2.x} \quad , \quad \omega_1\, \varphi_{1.y} + \omega_2\, \varphi_{2.y} \quad \text{and} \quad \omega_1\, \varphi_{1.w} + \omega_2\, \varphi_{2.w} \qquad (9)$$

in which the letters of (6) and (7) placed between parentheses have been omitted. Now liquid L will not change its composition any longer when

$$\frac{\omega_1\, \varphi_{1.x} + \omega_2\, \varphi_{2.x}}{x} = \frac{\omega_1\, \varphi_{1.y} + \omega_2\, \varphi_{2.y}}{y} = \frac{\omega_1\, \varphi_{1.w} + \omega_2\, \varphi_{2.w}}{1-x-y} \quad . \qquad (10)$$

is satisfied. These equations namely express that liq. L takes in (or gives off) the quantities of X, Y and W in the same ratio in which they are present already in liq. L; it is clear that the composition then will not change any more.

In (10) we now have 2 relations between the 3 variables x, y and P; if we now keep this pressure P constant, then x and y (viz. the composition of liquid L) have been determined. Besides it appears from this that during the further osmosis the quantity of the stat. liquid still is increasing or decreasing continuously. As these considerations obviously obtain not only for system (5), but also for (4), we now represent them by

$$\begin{array}{r|c|l} \multicolumn{1}{r}{M_1} & & \multicolumn{1}{l}{M_2} \\ inv\ i_1 & \begin{array}{c} stat.\ L\,(d) \\ P = const.\ \ \Delta m \gtreqless o \end{array} & inv\ i_2 \\ \multicolumn{1}{r}{\omega_1} & & \multicolumn{1}{l}{\omega_2} \end{array} \quad . \ . \ . \ . \ . \qquad (11)$$

in which we have indicated that the pressure P has been taken constant and that the quantity m of the stat. liquid may increase as well as decrease. It now follows from (10) that the composition of this stat. liquid depends upon:

1. the composition of the inv. liquids i_1 and i_2 and their pressures P_1 and P_2;
2. the nature of the two membranes and the ratio $\omega_1 : \omega_2$ of their surfaces;
3. the constant pressure P of the stationary liquid.

Further it appears that the composition of the stat. liquid is independent of the composition the variable liquid has at the beginning of the osmosis [1]).

---

[1]) For a closer consideration of the paths along which the var. liquid can travel during the osmosis and for some experimental examples comp..

F. A. H. SCHREINEMAKERS, These Proceedings **34**, 346 and 827 (1931).

F. A. H. SCHREINEMAKERS and J. P. WERRE, Rec. Trav. Chim. Pays-Bas **51**, 51, (1932).

F. A. H. SCHREINEMAKERS and H. H. SCHREINEMACHERS, These Proceedings **35**, 1241, (1932), and **36**, 629, (1933).

We now imagine the var. liquid closed up in a space with unstretchable or elastic walls [1]; we represent this by

$$\mathit{inv}\ i_1 \boxed{\;L\,(d)\;} \mathit{inv}\ i_2 \; . \; . \; . \; . \; . \; . \; . \; . \qquad (12)$$

Just as in Comm. I we again shall call this space a cell. If we now leave this system alone, liquid L will change its composition and quantity so that the pressure within the cell and its volume will change also. At a certain moment of the osmosis, however, a stationary state will occur, during which the composition and the pressure remain unchanged. As the volume of the cell will now also remain constant, liquid L through the one membrane must take in as much of each of the substances as it gives off through the other membrane. Then

$$\omega_1\,\varphi_{1.x} + \omega_2\,\varphi_{2.x} = 0 \quad \omega_1\,\varphi_{1.y} + \omega_2\,\varphi_{2.y} = 0 \quad \omega_1\,\varphi_{1.w} + \omega_2\,\varphi_{2.w} = 0 \quad (13)$$

must be satisfied.

As we now have 3 equations between x, y and P, the composition and the pressure of the stat. liquid have been determined; we shall call this pressure the stationary pressure. We now represent this stationary state by:

$$\mathit{inv}\ i_1 \begin{array}{|c|} \multicolumn{1}{l}{M_1 \qquad\qquad\qquad\qquad M_2} \\ \hline \textit{stat. } L\,(d) \\ P = \mathit{def.} \quad m = \mathit{def.} \\ \hline \multicolumn{1}{l}{\omega_1 \qquad\qquad\qquad\qquad \omega_2} \end{array} \mathit{inv}\ i_2 \; . \; . \; . \; . \; . \; . \qquad (14)$$

in which we have indicated that the pressure P as well as the quantity m have now been determined.

The composition and the pressure of this stationary liquid now depends upon:

1. the composition and the pressure of the liquids i_1 and i_2.
2. the nature of the two membranes and the ratio $\omega_1 : \omega_2$ of their surfaces.

If one or both membranes of (14) can stretch under the pressure, then ω_1 or ω_2 or both are also functions of P. To this should be added besides that now in consequence of the stretching also the permeability can change; what was said sub 2 then will obtain only for the nature and the ratio $\omega_1 : \omega_2$ as they are in the stationary state.

B. We now take the osmotic system

$$\mathit{inv}\ i_1 \mid m \times \mathit{stat}\ L\,(d+n) \mid \mathit{inv}\ i_2 \; . \; . \; . \; . \; . \; . \qquad (15)$$

in which m quantities of a stationary liquid, consisting of d substances,

---

[1] For equilibria in systems with elastic walls comp. F. A. H. SCHREINEMAKERS, These Proceedings **36**, 285, (1933).

which can diffuse through the two membranes and n non-diffusing substances 1)). If, for the sake of concentration we take the diffusing substances W, X and Y and the non-diffusing substances Z and U, we have the system

$$inv\ i_1 \mid m \times stat\ L\,(W + X + Y + \bar{Z} + \bar{U}) \mid inv\ i_2 \quad . \quad . \quad (16)$$

in which the small dashes placed over Z and U indicate that they do not diffuse. As we can represent the composition of this liquid L by

$$x\,X + y\,Y + z\,Z + u\,U + (1 - x - y - z - u)\,W. \quad . \quad . \quad (17)$$

it only contains 4 variables; if besides we add the quantity m and the pressure P, there will be 6 variables.

As the total quantity of each of the non-diffusing substances Z and U cannot change, we represent them by z_0 and u_0. We then have:

$$m\,z = z_0 \quad \text{and} \quad m\,u = u_0\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

As the stationary liquid contains non-diffusing substances, it is clear that its composition will only stop changing when its X-, Y- and W-amount remains constant; so of each of the substances X, Y and W as much must been taken in by the one membrane as has been given off by the other. Consequently the 3 equations (13) must be satisfied. So we now have 5 relations between the 6 variables x, y, z, u, m and P. If we now keep the pressure P constant, then the other variables viz. the quantity m and the composition of the stat. liquid have been completely determined.

As these considerations obtain not only for system (16), but also for (15), we now represent them by

$$inv\ i_1 \underset{\omega_1}{\overset{M_1}{\Bigg|}} \begin{array}{c} m \times stat\ L\,(d + n) \\ P = const. \quad m = def. \end{array} \underset{\omega_2}{\overset{M_2}{\Bigg|}} inv\ i_2 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

in which we have indicated that the pressure P has been taken constant and that the quantity m of the stat. liquid is completely defined. From this it appears that the quantity m and the composition of the stationary liquid depend upon:

1. the composition and pressure of the liquids i_1 and i_2;
2. the nature of the two membranes and the ratio $\omega_1 : \omega_2$ of their surfaces;
3. the constant pressure P of the stat. liquid;
4. the quantity of each of the non-diffusing substances.

We now imagine the stat. liquid of system (16) closed up in a cell; we

---

1) For equilibria in systems, in which non-diffusing substances may occur also, comp. F. A. H. SCHREINEMAKERS, These Proceedings **35**, 1038, 1131, 1235 (1932), **36**, 285 (1933).

shall call it system (16*a*). If we represent the volume of 1 quantity of liquid L by v, then the volume of the cell will be $m\ v$.

We shall first assume now that the membranes and the walls of the cell are unstretchable, so that the cell has a constant volume V, we then have:

$$m\,v = V \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

As v is a function of the pressure P and the composition (x, y, z and u), (20) represents a relation between the 6 variables.

If, however, the cell is elastically stretchable, 1) then a relation will exist between the volume V and the pressure within the cell, which we represent by

$$\varphi\,(P\,.\,V) = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

Here we assume that the volume of this cell under a definite pressure P is known. As $V = mv$, this also represents a relation between the 6 variables.

As of course the same 5 equations [viz. the 2 eq. 18 and the 3 eq. 13] obtain for this system (16*a*) besides, we now have 6 equations between the 6 variables x, y, z, u, m and P; the quantity m, the pressure P and the composition of the stat. liquid have consequently been determined.

As these considerations obtain not only for system (16*a*), but have general significance, we represent this stationary state by:

$$\begin{array}{ccc} & M_1 \qquad\qquad\qquad M_2 & \\ inv\ i_1 & \boxed{\begin{array}{c} m \times stat.\ L\ (d+n) \\ P = def. \quad m = def. \end{array}} & inv\ i_2 \\ & \omega_1 \qquad\qquad\qquad \omega_2 & \end{array} \quad . \; . \; . \; . \; . \quad (22)$$

in which we have indicated that the pressure and the quantity m of the stationary liquid are defined.

The quantity m, the pressure and the composition of this stat. liquid now depend upon:

1. the composition and the pressure of the liquids i_1 and i_2;
2. the nature of the two membranes and the ratio $\omega_1 : \omega_2$ of their surfaces;
3. the quantity of each of the non-diffusing substances;
4. the volume of the cell, that is to say the elasticity of the membranes and walls and its volume under a given pressure (e.g. at the beginning of the osmosis).

Of course these results obtain also for the special case that only water diffuses ($d = 1$); in every cell of the tissues discussed in Comm. I the

---

1) For equilibria in systems with elastic walls, comp. F. A. H. SCHREINEMAKERS l.c.

stat. liquid will consequently also have a definite pressure and composition, which may vary, however, from cell to cell.

C. For the general system

$$inv\ i_1 \mid m \times stat.\ L\,(d + d_1 + d_2 + n) \mid inv\ i_2 \quad . \quad . \quad . \quad (23)$$

now obtains, as the reader can easily deduce:

1. when $n = 0$, the same as for systems (11) and (14);
2. when $n \neq 0$, the same as for system (19) and (22).

whereby, however, we have to bear in mind that in the special case that $d = 0$, the stationary state is independent of the ratio $\omega_1 : \omega_2$; I shall refer to this later on.

D. Now we shall say that a liquid is "enclosed" when it has been closed up in a cell, viz. in a closed space, as has been discussed above for system (22), in other cases we shall say that the liquid is "open". This is the case e.g. when a liquid is in an open container or in a space, shut off by a movable piston, on which a constant pressure is brought to bear from the outside.

If we now imagine to be given:

a. the compositions and pressures of the inv. liquids;

b. the nature and the ratio of the surfaces of the membranes;

c. of a liquid, containing non-diffusing substances, also these quantities,

then we can summarise the preceding results in the following way:

1. when a stat. liquid is enclosed, its quantity, pressure and composition are completely defined (Syst. 14 and 22);
2. when a stat. liquid is open and is under a constant pressure, we distinguish 2 cases, namely:

α. if this liquid contains one or more non-diffusing substances, its quantity and composition are completely defined (Syst. 19);

β. if this liquid only contains diffusing substances, its composition is defined indeed, but its quantity will increase or decrease continuously and will only accidentally remain constant (Syst. 11).

From this we see that the quantity of a stationary liquid can increase or decrease continuously only then when it is "open" and contains diffusing substances only; every other stat. liquid (open or enclosed) does not change its quantity.

(To be continued.)

Leiden, Lab. of Inorganic Chemistry.