Chemistry. — *Osmotic systems, in which non-diffusing substances may occur also.* III. *Equilibria with one invariant liquid.* By F. A. H. SCHREINEMAKERS.

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

We take the osmotic system

$$(L)_P \mid inv.\ L_i\,(d+n')_{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which on the left side of the membrane a variable liquid L under a pressure P is found; on the right side is an invariant liquid L_i, containing d diffusing and n' non-diffusing substances, under the constant pressure P_i.

We are able during our experiment to keep the composition of this liquid i practically invariant, e.g. by refreshing it continuously or at short intervals, or by leading a continuous current of this liquid along the membrane, etc.

In living nature corresponding systems may occur, when on one of the sides of the membrane there flows a liquid (blood, etc.) or when a tissue is present, keeping practically the same composition.

Now we assume that system (1) is in equilibrium when the variable liquid has a composition L_e and a pressure P_e; we represent this equilibrium by:

$$(L_e)_{P_e} \mid inv.\ L_i\,(d+n')_{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This liquid e now will contain the same d diffusing substances as liquid i. If namely one or more of these d diffusing substances was or were not yet present in liquid L of (1), they will yet enter into that liquid during the osmosis. If in liquid L there were also other diffusing substances than in liquid i, they will divide themselves between the two liquids; as, however, liquid i is kept invariant, these substances are being taken away continuously, so that they will have disappeared completely from the system at last.

When liquid L of (1) contains n non-diffusing substances, then these will of course also be present in liquid L_e; of course the n' non-diffusing substances of liquid i cannot force their way through the membrane either. From this it appears that we now may represent equilibrium (2) by

$$L_e\,(d+n)_{P_e} \mid inv.\ L_i\,(d+n')_{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equilibrium would have $d+n+n'$ freedoms (comp. B Comm. I) when the right-side state was not invariant; as the number of freedoms decreases because of this with $d + n'$ ($d + n' - 1$ concentrations namely and the pressure P_i are kept constant) n freedoms still remain, relating only to the composition and the pressure of liquid e.

If for the sake of simplicity we now call the right-side state the i- and the left side state the e-state, then we may say:

A. the e-state of equilibrium (3) has n freedoms, viz. as many freedoms as there are non-diffusing substances in liquid e.

We see that at once also in the following way. The e-state is determined by $d + n$ variables (namely the $d + n - 1$ concentrations and the pressure of liquid e). As (3) is in equilibrium, however, d relations

$$(O\,A)_e = (O\,A)_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

will exist between these variables, expressing that each of the d diffusing substances must have the same $O.A.$ on both sides of the membrane; so there are only n free variables.

Each of the d equations (4) contains the pressure and composition of each of the two liquids; from this it appears that pressure and composition of liquid e will depend not only upon the diffusing substances, but also on all non-diffusing substances on the left and right sides of the membrane.

In the special case that on the left side no non-diffusing substances are present, (3) passes into:

$$L_e\,(d)_{P_e} \mid inv.\; L_i\,(d + n')_{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As now $n = 0$, the e-state has not one freedom left. We are able to deduce that now $P_e < P_i$ always. From this it follows:

B. when liquid e does not contain any non-diffusing substances, then the e-state has not got a freedom left, the pressure and the composition of liquid e are completely determined then; the pressure P_e is always smaller than P_i. In the special case that liquid i has not got non-diffusing substances either, both liquids have the same composition and pressure (comp. *E* Comm. I).

If there are no non-diffusing substances on the right side, then (3) passes into:

$$L_e\,(d + n)_{P_e} \mid inv.\; L_i\,(d)_{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which now $P_e > P_i$ always. We now find:

C. when liquid i does not contain any non-diffusing substances, then an ∞ number of e-states can exist, having n freedoms; the pressure P_e can have an ∞ number of values, but is always greater than P_i.

When $n = 1$, then one definite composition of liquid e belongs to every pressure P_e; when $n > 1$ then liquid e can still have an ∞ number of compositions with every pressure P_e.

In the preceding communications we have also discussed Def. Q.-equilibria (systems), namely equilibria containing a definite quantity of each of the substances; such equilibria, however, can only exist here in a more limited meaning.

If e.g. we take system (1), it will no longer contain a definite quantity of the d diffusing and n' non-diffusing substances, because we must keep liquid i invariant (e.g. by continuously refreshing liquid i); however, the quantity of each of the non-diffusing substances on the left side of the membrane, cannot change.

If, therefore, we put a definite quantity of each of the non-diffusing substances on the left side of the membrane into system (1), then the same quantities will be present also in the equilibria (2) and (3) on the left side of the membrane.

Now it is clear that we may not speak any more of a Def. Q.-equilibrium, but only of an equilibrium (system) containing a definite quantity of every non-diffusing substance on the left side of the membrane. We shall call it a "onesided Def. Q.-equilibrium".

We now represent the onesided Def. Q.-equilibrium (3) by

$$m \times L_e\,(d+n)_{P_e} \mid inv.\ L_i\,(d+n')_{P_i} \quad \ldots\ldots \quad (7)$$

in which m quantities of liquid e are present. If we now represent the total quantity of each of the n non-diffusing substances by $(u_1)_0$, $(u_2)_0$ etc. and the concentrations of these substances in liquid e by u_1, u_2 etc., we have the n relations:

$$m\,u_1 = (u_1)_0 \ , \ m\,u_2 = (u_2)_0 \ , \ etc. \quad \ldots\ldots \quad (8)$$

We now have on the e-side of (7), $d+n+1$ variables, namely the $d+n-1$ concentrations, the pressure and the quantity m of liquid e; as between these variables the d relations (4) and the n relations (8) exist there is only one free variable left. From this it follows:

D. a onesided Def. Q.-equilibrium can have an ∞ number of e-states with one freedom; we can still give an ∞ number of values to the pressure P_e, but to every pressure belongs a definite composition and quantity m of liquid e.

If we now assume besides that the pressure P_e has a definite value then (7) is a onesided Def. *P.Q.*-equilibrium; from the above then follows:

E. the e-state of a onesided Def. *P.Q.*-equilibrium is completely determined, so that the quantity m and the composition of liquid e are completely determined (comp. also *L.* Comm. I).

We now imagine the m quantities of liquid e shut up in a space with a volume V; we now represent this by

$$[m \times L_e\,(d+n)_{P_e}]_V \mid inv.\ L_i\,(d+n')_{P_i} \quad \ldots\ldots \quad (9)$$

If we now take a definite volume V, then we shall call (9) a onesided Def. $V.Q.$-equilibrium (comp. also Comm. I).

Above we have seen that the e-side contains $d+n+1$ variables; between them, however, the d relations (4), the n relations (8) exist and further the relation:

$$m\,v = V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which v represents the volume of one quantity of liquid e. As v is a function of pressure and composition of liquid e, so (10) contains all variables of the e-side of (9). As we now have $d+n+1$ relations between the $d+n+1$ variables, it follows:

F. the e-state of a onesided Def. $V.Q.$-equilibrium is completely determined, so that the quantity m, the pressure P_e and the composition of liquid e are completely determined.

Above in E and F we have seen that the e-state of a onesided Def. $P.Q.$- and $V.Q.$-equilibrium is completely determined. This e-state, however, depends upon the i-state; this appears from the d equations (4), all containing in their second part the concentrations and the pressure of liquid i.

From the preceding considerations it now follows at once:

G_1) every change of the i-state of a onesided Def. $P.Q.$-equilibrium causes a change of its e-state, namely of the quantity and composition of liquid e.

G_2) each change of the i-state of a onesided Def. $V.Q.$-equilibrium causes a change of its e-state, namely of the quantity, composition and pressure of liquid e.

Instead of liquid e we can also imagine some tissue e in osmotic equilibrium, with a liquid i flowing along it. Every change of the composition or pressure of this liquid i then also will cause a change of the state of tissue e.

If that tissue is under a constant pressure, then only the quantity and the composition of the liquid in e will consequently change (comp. G_1); when this tissue is shut up in a non-elastic film, so that its volume remains constant, then not only the quantity and the composition of the liquid in e will change, but also its pressure (comp. G_2).

This still obtains when the film is elastic; later on I shall refer to this case again.

In communication II the influence has been discussed which the change in the permeability of a membrane may have on the state of an equilibrium. In accordance with what went before (A, B and e Comm. I) we now find:

H_1) when the membrane of a onesided Def. $P.Q.$- or $V.Q.$-equilibrium remains equipermeable or becomes less permeable, then its e-state does not change.

H_2) when the membrane of a onesided Def. $P.Q.$- or $V.Q.$-equilibrium becomes more or m.l. permeable, the e-state will change; every change is followed by an osmosis until the new e-state has set in.

Here the same remark obtains of course as with B in Comm. II.

In order to discuss some examples more in detail, we take the onesided Def. $P.Q.$-equilibrium

$$m \times L_e\,(d + \overline{X} + \overline{Y})_{P_e} \mid inv.\ L_i\,(d + \overline{X} + \overline{Z})_{P_i} \quad . \quad . \quad . \quad (11)$$

Here it depends upon the concentrations of the substances whether P_e will be smaller or greater or accidentally equal to P_i.

1. When the membrane of (11) becomes permeable for X, we get:

$$m' \times L'_e\,(d + X + \overline{Y})_{P_e} \mid inv.\ L_i\,(d + X + \overline{Z})_{P_i} \quad . \quad . \quad , \quad (12)$$

in which the quantity m' and the composition of liquid e are different now from what they were in (11).

2. When the membrane of (11) becomes permeable for Y, this substance Y will diffuse also towards the right, where it is taken away continuously until it has completely disappeared from the system at last. Then we have the equilibrium

$$m' \times L'_e\,(d + \overline{X})_{P_e} \mid inv.\ L_i\,(d + \overline{X} + \overline{Z})_{P_i} \quad . \quad . \quad . \quad . \quad (13)$$

in which the quantity m' and the composition of liquid e are different from what they were in (11).

3. When the membrane of (11) becomes permeable for Z, then

$$m' \times L'_e\,(d + \overline{X} + \overline{Y} + Z)_{P_e} \mid inv.\ L_i\,(d + \overline{X} + Z)_{P_i} \quad . \quad . \quad (14)$$

forms.

4. When the membrane becomes permeable for Y and Z, then after the disappearance of the substance Y, (11) passes into:

$$m' \times L'_e\,(d + \overline{X} + Z)_{P_e} \mid inv.\ L_i\,(d + \overline{X} + Z)_{P_i} \quad . \quad . \quad . \quad (15)$$

In both these equilibria the quantity m' and the composition of liquid e are different from what they were in (11).

5. When the membrane becomes permeable for X and Y, the substance Y will disappear from the system. We then get a system

$$m' \times L'_e\,(d + X)_{P} \mid inv.\ L_i\,(d + X + \overline{Z})_{P_i} \quad . \quad . \quad . \quad . \quad (16)$$

which can only be in equilibrium, however, when the new liquid e has a pressure completely determined and which is represented in (16) by P.

So we have a condition here, which needed not to be satisfied in the preceding equilibria (11)—(15); this results from the fact that in these equilibria there is at least one non-diffusing substance on both sides of the membrane. In (16) liquid e, however, does not contain a non-diffusing substance any more; from B it now follows that P must have a completely determined value, which is smaller than P_i.

When now pressure P_e of (11) does not happen to be equal to pressure

P, which is necessary to produce an equilibrium in (16), then no equilibrium

$$m' \times L'_e\,(d + X)_{Pe} \mid inv.\ L_i\,(d + X + \overline{Z})_{Pi} \quad . \quad . \quad . \quad . \quad (17)$$

can exist and consequently something else must take place. We now distinguish two cases.

a. $P_e > P$. Liquid e will completely disappear in the invariant liquid i; we then get

$$\times_{Pe} \mid inv.\ L_i\,(d + X + \overline{Z})_{Pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

in which the sign $\times$ indicates that liquid e has completely disappeared.

b. $P_e < P$. The quantity of liquid e will continuously increase; we represent this by

$$\uparrow_{Pe} \mid inv.\ L_i\,(d + X + \overline{Z})_{Pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

in which the arrow pointing upwards indicates that the quantity of liquid e increases continuously.

6. When the membrane becomes permeable for X and Z, we get a system

$$m' \times L'_e\,(d + X + \overline{Y} + Z)_P \mid inv.\ L_i\,(d + X + Z)_{Pi} \quad . \quad . \quad (20)$$

which, as liquid i now does not contain non-diffusing substances any more, can be in equilibrium under an ∞ number of pressures P, which must all be greater than P_i, however; to every pressure P belongs one definite liquid e (comp. C). We now distinguish two cases.

a. $P_e > P_i$. As the pressure P_e of (11) is greater now than P_i, (11) will now pass into the equilibrium

$$m' \times L'_e\,(d + X + \overline{Y} + Z)_{Pe} \mid inv.\ L_i\,(d + X + Z)_{Pi} \quad . \quad . \quad (21)$$

in which the quantity and the composition of liquid e are different from what they were in (11).

b. $P_e < P_i$. As the pressure P_e of (11) is smaller now than P_i, no equilibrium (20) can exist; we then get a system

$$\uparrow_{Pe} \mid inv.\ L_i\,(d + X + Z)_{Pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

in which the quantity of liquid e increases continuously.

7. When the membrane becomes permeable for X, Y and Z, the substance Y will disappear from the system; we then get a system

$$m' \times L'_e\,(d + X + Z)_P \mid inv.\ L_i\,(d + X + Z)_{Pi} \quad . \quad . \quad . \quad (23)$$

which, because all substances diffuse, is only then possible when $P = P_i$ and both liquids have the same composition. We now distinguish again two cases.

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

$$\times_{P_e} \mid inv.\ L_i\,(d + X + Z)_{P_i} \quad \ldots\ldots \quad (24)$$

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

$$\uparrow_{P_e} \mid inv.\ L_i\,(d + X + Z)_{P_i} \quad \ldots\ldots \quad (25)$$

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.

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I. *Introduction.*

We take an osmotic system

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

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

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