Chemistry. — *Equilibria in osmotic systems in which forces act.* I.
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In deducing and discussing the phenomena which may obtain with the osmosis, we have until now assumed that the membrane is "inactive" in this respect namely that no forces act in it, capable of driving one or more of the substances in some direction or other. When such forces do occur, as may be the case e.g. in living membranes [1]), we shall call the membrane "active".

It is also possible to imagine that such driving forces are present in the liquids themselves; then we shall call these liquids "active" also.

Osmotic systems with an active membrane, permeable for one substance only.

We suppose in the osmotic system:

$$L \mid L' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

first an inactive membrane $M(W)$ viz. a membrane, in which no forces act and which is permeable for water only. For this obtains, as we have deduced already before:

A. the water diffuses towards that side of an inactive membrane $M(W)$, where the O.W.A. (osmotic-water-attraction) is greatest. When both liquids have the same O.W.A., no water diffuses

From this it appears that the direction in which the water diffuses through an inactive membrane $M(W)$, is determined only by the O.W.A. of the two liquids, consequently by their composition and their pressure; so the nature of the membrane does not influence the direction, in which the water moves. Consequently we may say also:

B. the nature of the inactive membrane $M(W)$ plays no part with respect to the direction in which the water diffuses: this is determined only by the O.W.A. of the two liquids.

We now suppose in the osmotic system:

$$\left.\begin{array}{c} \longleftarrow F \\ L \mid L' \\ \longleftarrow \delta a \ mol \ W \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1]) Compare e.g. J. STRAUB, Rec. Trav. Chim. Pays-Bas **48**, 49 (1929).

an active membrane $M(W)$ in which a force F works towards the left; first we still assume with this that all processes cohaerent with this force, are reversible; later on we shall refer to the meaning of this and the other suppositions. We represent the work, performed by this force, when 1 mol. water diffuses towards the left, by E. If we now suppose that $\delta\alpha$ mol. water diffuse towards the left, as we have assumed in (2), then this force performs a work $E\,.\,\delta\alpha$ on the system. Reversally we may also say now that the system performs an external work $-E\,.\,\delta\alpha$.

We now represent the free energy of the two liquids by ψ and ψ'; their thermodynamical potentials by Z and Z', their volumina by V and V' and their pressures by P and P'.

If the volumina V and V' of the two liquids are now kept constant, then with this diffusion of $\delta\alpha$ mol. water, the free energy

of liquid L increases with $\left(\frac{\delta\psi}{\delta\alpha}\right)_v \delta\alpha$

and of liquid L decreases with $\left(\frac{\delta\psi'}{\delta\alpha}\right)_{v'} \delta\alpha$.

As, according to a well-known thesis of GIBBS, the free energy, to which the external work, performed by the system, is added, can only decrease or remain constant,

$$\left[\left(\frac{\partial\psi}{\partial\alpha}\right)_v - \left(\frac{\partial\psi'}{\delta\alpha}\right)_{v'} - E\right]\delta\alpha \leqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

must be satisfied.

We now represent, in the same way as before:

$$\left(\frac{\partial\psi}{\partial\alpha}\right)_v = -\xi \quad \text{and} \quad \left(\frac{\partial\psi'}{\delta\alpha}\right)_{v'} = -\xi' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

sa that ξ and ξ' represent the O.W.A.'s of the liquids L and L'. It follows from (3) that

$$[\xi - \xi' + E]\,\delta\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

must be satisfied now.

Above we have assumed that with the diffusion of $\delta\alpha$ mol. water, the volumina V and V' remain constant; if, however, the pressures P and P' are kept constant, then the free energy of the system increases with:

$$\left[\left(\frac{\partial\psi}{\partial\alpha}\right)_P - \left(\frac{\partial\psi'}{\partial\alpha}\right)_{P'}\right]\delta\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

As the volume of liquid L now increases with $\left(\frac{\partial v}{\partial\alpha}\right)_P \delta\alpha$ and that of liquid L' decreases with $\left(\frac{\partial v'}{\partial\alpha}\right)_{P'} \delta\alpha$, the system will now not only perform the work $-E\,\delta\alpha$, but:

$$\left[P\left(\frac{\partial v}{\partial\alpha}\right)_P - P'\left(\frac{\partial v'}{\partial\alpha}\right)_{P'} - E\right]\delta\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

As $\psi + pv = Z$ and $\psi' + p'v' = Z'$, it follows from (6) and (7):

$$\left[\left(\frac{\partial Z}{\partial a}\right)_P - \left(\frac{\partial Z'}{\partial a}\right)_{P'} - E\right] \delta a \leqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we now take again:

$$\left(\frac{\partial Z}{\partial a}\right)_P = -\xi \quad \text{and} \quad \left(\frac{\partial Z'}{\partial a}\right)_{P'} = -\xi' \quad . \quad . \quad . \quad . \quad . \quad (9)$$

then follows

$$[\xi - \xi' + E]\, \delta a \geqq 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which is in accordance with (5). In the special case that $E = 0$ and the membrane consequently is inactive, (10) passes into:

$$[\xi - \xi']\, \delta a \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

from which the rules A and B, mentioned above, have already been deduced before.

To make a simple formulation of (10) possible, we shall first introduce the notions "internal" and "active" O.W.A. of a liquid, also on account of our future discussion of active liquids.

When in system (2) 1 mol. water diffuses from L' towards L, then force F performs a work E; for the sake of simplicity we now shall say that each mol. water in liquid L' has a potential energy E with respect to the water in liquid L.

We now may say that two factors are at work in liquid L'. of which one attracting the water and the other expelling the water.

One factor is the O.W.A. $= \xi'$, determining the attraction of the water or keeping it in L'. As this O.W.A. depends only upon the internal state of the liquid (composition and pressure) we shall call this the "internal" O.W.A.

The second factor is the potential energy E the water has in liquid L'; this E tries to expel the water out of liquid L' and, therefore, works in a direction opposite to that of the internal O.W.A. $= \xi'$ of this liquid.

Generally speaking we shall now call the internal O.W.A. of a liquid (gas etc.) diminished by its potential energy, the "active" O.W.A. So we may put in general:

active O.W.A. = internal, O.W.A. — pot. energy.

When a liquid (gas etc.) has no potential energy, then we have, therefore:

active O.W.A. = internal O.W.A.

so that both these O.W.A.'s are equal now.

In future we shall, for the sake of simplicity, always speak of the "active" O.W.A., also when the active and the internal O.W.A. are equal.

For liquid L of system (2) obtains therefore:

$$\text{active O.W.A.} = \xi$$

and for liquid L' of this system:

$$\text{active O.W.A.} = \xi' - E.$$

Above we have seen that the quantity of water δa, diffusing towards the left in system (2), must satisfy (10); we now distinguish three cases.

a. $\xi > \xi' - E$. As the coefficient of δa in (10) is positive now, δa must be positive also; this means that the water in system (2) now diffuses towards the left. If we consider the meanings of ξ and $\xi' - E$ then it appears that the water diffuses towards that side of the membrane, where the active O.W.A. is greatest.

b. $\xi < \xi' - E$. As the coefficient of δa is negative now, δa must be negative also; consequently the water now diffuses towards the left, therefore, again towards that side of the membrane where the active O.W.A. is greatest.

c. $\xi = \xi' - E$. As the coefficient of δa is now zero, we must introduce also higher powers of δa in (10); we now find:

$$-Q\,(\delta a)^2 \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which Q is positive. As $(\delta a)^2$ is positive for every positive or negative value of δa and the first part of (12) consequently negative, (12) can only be satisfied by $\delta a = 0$; consequently no water passes through the membrane.

Summarising these results, it follows:

C. the water diffuses towards that side of the active membrane $M(W)$, where the active O.W.A. is greatest; when the two liquids have the same active O.W.A., no water will diffuse.

In the special case that no forces act in the membrane, so that the active O.W.A. of the two liquids is the same as the internal O.W.A., rule *C* passes into *A*.

As the preceding considerations obtain not only for water, but also for an arbitrary substance *S*, and as we may look upon an inactive membrane as a special case of an active membrane, we may consequently say also:

D. a substance *S* diffuses towards that side of a membrane $M(S)$ [active or inactive] where the active O.S.A. is greatest;

when the two liquids (gas etc.) have the same O.S.A., then the substance *S* does not diffuse;

so the nature of this membrane [active or inactive] does not influence the direction, in which the substance *S* will diffuse.

Previously in discussing the osmosis we have distinguished a "congruent" and an "incongruent" direction; we have stated namely:

E. a substance S diffuses congruently when it goes from smaller towards greater internal O.S.A. The opposite direction (consequently from greater towards smaller O.S.A.) is called incongruent.

In the special case that we have an inactive membrane, permeable for one substance only, follows:

F. a substance S diffuses through all inactive membranes $M(S)$ in the same, viz. in congruent direction.

It is clear that this rule obtains no more, however, when this membrane is active; from our previous considerations then follows:

G. a substance S can diffuse through an active membrane $M(S)$ congruently as well as incongruently. In this case the direction of the diffusion namely is not defined by the "internal" but by the "active" O.S.A. of the two liquids (gases etc.).

In order to apply the preceding considerations to some simple cases, we suppose in the osmotic system:

$$\begin{array}{c|c|c} L & & L' \\ & M(W) & \\ \xi & & \xi' \end{array} \qquad \xi < \xi' \longrightarrow W \quad . \quad . \quad . \quad (13)$$

an inactive membrane $M(W)$. If, for the sake of concentration, we take $\xi < \xi'$, then the water will diffuse towards the right; so the arrow indicates also the congruent direction of the water in system (13).

We now suppose the inactive membrane (13) replaced by an active one, which performs a work E on each mol. water diffusing towards the left; we represent this system by

$$\begin{array}{c|c|c} \multicolumn{3}{c}{\longleftarrow E} \\ L & & L' \\ & M(W) & \\ \xi & & \xi' - E \end{array} \qquad \left.\begin{array}{l} \xi < \xi' - E \longrightarrow W \\ \xi = \xi' - E \text{ —— } 0\, W \\ \xi > \xi' - E \longleftarrow 0\, W \end{array}\right\} \quad . \quad (14)$$

in which ξ and $\xi' - E$ are the active O.W.A.'s.

Now it is clear that it depends upon the value of E whether ξ will be smaller than, equal to, or larger than $\xi' - E$; consequently we may distinguish the three cases indicated in (14).

So a certain value of E viz. $E = \xi' - \xi$ exists, in which case no water diffuses; with a smaller value of E is $\xi < \xi' - E$ and consequently the water goes towards the right; with a greater value of E the water goes towards the left. In order to indicate that this second direction is incongruent, the sign 0 has been placed in (14) beside this second arrow.

In the special case that $E = \xi - \xi'$, no water diffuses through the active membrane, whereas it does diffuse through the inactive one; we may also call this non-diffusion of water incongruent now.

If we replace the active membrane of (14) by an other membrane, in which the force acts towards the right, then we represent this by:

$$\begin{array}{r|c|l} & \xrightarrow{\quad\quad} E & \\ L & & L' \\ & M(W) & \\ \xi - E & & \xi' \end{array} \qquad \left.\xi - E < \xi' \longrightarrow W\right\} \quad . \quad (15)$$

in which the active O.W.A. now is $\xi - E$ and ξ'. As has been assumed $\xi < \xi'$, $\xi - E$ is always smaller than ξ'; consequently in system (15) the water will always diffuse towards the right and, therefore, congruently.

If we compare the systems (13), (14) and (15) and if we take into consideration that the force in system (14) acts in incongruent direction and in system (15) in congruent direction, we see that only a force, acting in incongruent direction can alter the direction of diffusion of a substance.

We can imagine, as may be the case perhaps with living membranes, that E is dependent on all sorts of factors, acting on the membrane, e.g. temperature (light, hysteresis etc.). If we consider system (14) then it becomes clear that we can say:

H. when in a membrane the force acts in incongruent direction and the E changes with the temperature, then the direction, in which a substance diffuses, may be dependent on the temperature.

Of course the same may obtain also for a change in the other factors, e.g. light, age etc.

We now take the special case that the liquid L of system (13) consists of pure water; we then have the osmotic system:

$$\begin{array}{r|c|l} \textit{water} & & L' \\ & M(W) & \\ \xi & & \xi' \end{array} \qquad \left.\xi < \xi' \longrightarrow W\right\} \quad . \; . \; . \quad (16)$$

in which $\xi < \xi'$, so that the water must diffuse towards the right. Instead of (14) we then get the system:

$$\begin{array}{r|c|l} & \xleftarrow{\quad\quad} E & \\ \textit{water} & & L' \\ & M(W) & \\ \xi & & \xi' - E \end{array} \qquad \left.\begin{array}{l} \xi < \xi' - E \longrightarrow W \\ \xi = \xi' - E \text{——} 0\ W \\ \xi > \xi' - E \longleftarrow 0\ W \end{array}\right\} \quad . \quad (17)$$

It now depends upon the value of E, whether the water will diffuse towards the solution or from the solution towards the pure water. If we represent the value of E in case no water diffuses, by E_0, then E_0 is consequently determined by:

$$E_0 = \xi' - \xi \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

For L' we now take a binary liquid with the composition:

$$x \; mol \; X + (1 - x) \; mol \; W \quad \ldots \ldots \quad (19)$$

We then may write for (18):

$$E_0 = \int_0^x \frac{\partial \zeta'}{\partial x} \, dx \quad \ldots \ldots \ldots \quad (20)$$

If we represent the thermodynamical potential of 1 quantity of L by Z, we have:

$$\xi' = - Z + x \frac{\partial Z}{\partial x} \quad \text{and} \quad \frac{\partial \zeta'}{\partial x} = x \frac{\partial^2 Z}{\partial x^2} = xr \quad \ldots \quad (21)$$

Instead of (20) then follows:

$$E_0 = \int_0^x xr \, dx \quad \ldots \ldots \ldots \quad (22)$$

so that E_0 has been determined. From this follows for small values of x:

$$E_0 = RTx \quad \ldots \ldots \ldots \quad (23)$$

so that for small values of x, E_0 is proportionate to the concentration of the non-diffusing substance.

When e.g. in system (17) L' is a diluted solution, then for $E < RTx$ the water will diffuse towards the solution and for $E > RTx$ from the solution towards the pure water.

Of course it is also possible to connect E_0 with the osmotic pressure and the O.W.V.P. (osmotic-water-vapour-pressure) of liquid L'; I shall refer to this later on.

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