Es ist klar, dass eine derartige Feldtheorie nicht die BORN'sche Wahrscheinlichkeitsdeutung des ψ Feldes uebernehmen kann, und es bleibt also einstweilen eine offene Frage, ob eine solche Theorie eine widerspruchslose Deutung der atomistischen Struktur der Materie ueberhaupt zulaesst.

Chemistry. — *Stationary, checked and other states of osmotic systems.* I.
By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of May 27, 1933).

1. *Introduction.*

If we imagine in the osmotic system:

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

a membrane $M(W)$, i.e. a membrane permeable for water only, then the water will diffuse from the liquid with the smaller—towards that with the greater $O.W.A.$ and this osmosis will continue until both liquids have got the same $O.W.A.$. It does not matter here of what substances these liquids consist and what compositions they have.

In order to make it easier to represent some of the systems to be discussed later on and to simplify the discussions, I shall now indicate the $O.W.A.$ of a liquid by a number I shall take the greater, the greater the $O.W.A.$ of this liquid will be. If e.g. I shall say that liquid L has an $O.W.A. = 10$ and liquid L' an $O.W.A. = 20$, I mean nothing by this but to say that L' has a greater $O.W.A.$ than L; in the osmotic system:

$$L(10) \mid L'(20) \quad \rightarrow W \quad \ldots \ldots \ldots \quad (2)$$

in which the numbers now indicate the $O.W.A.$, the water will consequently diffuse through a membrane $M(W) \rightarrow$. However, these numbers have no other, real meaning here, and e.g. they certainly do not mean to say that liquid L' would have $2 \times$ as great an $O.W.A.$ as liquid L.

Of course we might choose numbers with a more real theoretical or practical meaning; I am only going to say a few words in explanation of the second case.

Previously we have deduced among other things:

a. if we take water away from a liquid, then its $O.W.A.$ will become greater; if we add water to a liquid, its $O.W.A.$ will become smaller.

For a binary liquid, consisting of water and a substance X, it follows from this:

b. the $O.W.A.$ of a binary liquid increases in proportion to the quantity of its X-amount.

This follows at once from *a*, because the W-amount of a binary liquid decreases, when its X-amount increases.

So an aqueous solution of 20 % of sugar will have a greater $O.W.A.$ than a solution of 15 % ; the latter in its turn will have a greater $O.W.A.$ than a solution of 10 % of sugar and this again a greater $O.W.A.$ than pure water. Of course the same obtains also for aqueous solutions of alcohol, $NaCl$ and any other substance.

Now we take e.g. an osmotic system :

$$L \mid (W + sugar) \quad \ldots \ldots \quad (3)$$

in which on the right side of the membrane $M(W)$ is an aqueous solution of sugar. Now the water will diffuse $\rightarrow$ or $\leftarrow$, according to the liquid on the right side or on the left side of the membrane having the greater $O.W.A.$; when the two liquids have the same $O.W.A.$, then no water will run through the membrane.

If now in the osmotic system :

$$L_1 \mid (W + 10\,\% \; sugar) \qquad - W \quad \ldots \quad (4)$$

in which the right-side solution contains 10 % of sugar, no water diffuses, then liquid L_1 no matter out of how many and out of what substances it consists, consequently has the same $O.W.A.$ as an aqueous solution of 10 % of sugar.

When in the osmotic systems

$$L_2 \mid (W + 15\,\% \; sugar) \qquad - W \quad \ldots \quad (5)$$

and

$$L_3 \mid (W + 20\,\% \; sugar) \qquad - W \quad \ldots \quad (6)$$

no water diffuses either, then liquids L_2 and L_3 will respectively have the same $O.W.A.$ as aqueous solutions of 15 and 20 % of sugar.

If we now indicate the $O.W.A.$ of these liquids L_1, L_2 and L_3 by the numbers 10, 15 and 20, then these numbers will now have a real meaning indeed.

Of course we could also take a solution of any other substance instead of the solution of sugar; then, however, the numbers would become different and no more have the ratio 10 : 15 : 20. We shall attach no further meaning, however, to these numbers by which we shall henceforth indicate the $O.W.A.$, than that a greater number indicates that the $O.W.A.$ is greater.

2. *Stationary states in systems with membranes, permeable for water only.*

In the osmotic system :

$$inv\,(i) \underset{\omega_1}{\mid} L \underset{\omega_2}{\mid} inv\,(i_1) \quad \ldots \ldots \ldots \quad (7)$$

there are two invariant liquids i and i_1, a variable liquid L and two membranes with the surfaces ω_1 and ω_2. As we shall begin by assuming besides that both membranes are permeable for water only, it is of no importance for our further considerations whether these three liquids contain the same substances yes or no. We can keep the liquids i and i_1, practically invariant by refreshing them at short intervals during the osmosis or by conducting a current of these liquids along the membranes.

As the two membranes are permeable for water only, so that the variable liquid can only take in or give off water, the concentrations of the substances X, Y, Z etc. present in it, will, therefore, change continuously during the osmosis in such a way that their ratio remains the same. Consequently, when in system (7) we start from a definite liquid L, we only have to consider its W-amount as an independent variable.

If we now leave system (7) alone, the variable liquid will at last get a definite composition, which will not change any more during the further osmosis; then a stationary state has set in, which we represent by:

$$inv\,(i) \underset{\omega_1}{\overset{M_1}{|}} stat.\ L \underset{\omega_2}{\overset{M_2}{|}} inv\,(i_1) \qquad \underset{\rightarrow W \rightarrow}{} \quad \ldots\ldots\ldots \quad (8)$$

Then the same quantity of water will flow through the one membrane as through the other, so that not only the composition but also the quantity of the stationary liquid will change no more. If for the sake of concentration we assume that liquid i_1, has a greater $O.W.A.$ than liquid i, the water will diffuse according to the arrows in (8).

In order to elucidate this we imagine that per second γ_1 and γ_2 quantities of water diffuse $\rightarrow$ through 1 cM^2 of the membranes M_1 and M_2 respectively; then liquid L will change no more, when

$$\omega_1 \gamma_1 = \omega_2 \gamma_2 \quad \ldots\ldots\ldots \quad (9)$$

The quantity γ_1 depends upon the composition of liquid i and the W-amount $= w$ of liquid L; the quantity γ_2 depends upon the composition of liquid i_1 and the W-amount $= w$ of liquid L; consequently we may put:

$$\gamma_1 = \varphi_1 (i.\ w) \quad \text{and} \quad \gamma_2 = \varphi_2 (w.\ i_1) \quad \ldots\ldots \quad (10)$$

in which φ_1 besides contains the magnitudes, determining the nature of the membrane M_1 and φ_2 those of M_2. It now appears from (9) and (10) that

$$\omega_1 \varphi_1 (i\ w) = \omega_2 \varphi_2 (i_1\ w) \quad \ldots\ldots\ldots \quad (11)$$

must be satisfied, so that the W- amount $= w$ and also, therefore the composition of the stationary liquid L has been completely determined. From this it follows that the composition of the stationary liquid depends upon:

1^0. the compositions of the invariant liquids i and i_1.

2^0. the nature of the two membranes and the ratio $\omega_1 : \omega_2$ of their surfaces.

3^0. the ratio of the concentrations of the substances X, Y, Z etc. in the original variable liquid, which is the same in the stational liquid of course.

Later on we shall see that what has been mentioned sub 3 does not play a part, when the membranes are permeable for all substances.

Corresponding considerations obtain also for systems with 2 and more variable liquids. If e.g. we leave to itself the system:

$$\underset{\longrightarrow}{\textit{inv}\ i \underset{\omega_1}{|}} \ \underset{\longrightarrow}{L_1 \underset{\omega_2}{|}} \ \underset{\longrightarrow}{L_2 \underset{\omega_3}{|}} \ \underset{\longrightarrow}{L_3 \underset{\omega_4}{|}} \ \underset{\longrightarrow}{L_4 \underset{\omega_5}{|}} \ \textit{inv}\ i_1 \ W \quad \ldots\ldots \quad (12)$$

then a stational state will set in here also, in which the same quantity of water will flow through each of the 5 membranes, so that not only the composition, but also the quantity of each of these 4 liquids will change no more. The W-amount and consequently also the composition of each of these 4 liquids is defined by the 4 equations:

$$\omega_1 \gamma_1 = \omega_2 \gamma_2 = \omega_3 \gamma_3 = \omega_4 \gamma_4 = \omega_5 \gamma_5 \quad \ldots\ldots \quad (13)$$

in which γ_1, γ_2 etc. represent similar functions as in (10).

We may also extend these considerations to systems in which the liquids are in any way in contact with one another as e.g. in the system:

u	v	w	m	p	q
z	i	x	y	i_1	r

. . . . . (14)

Here we find besides the invariant liquids i and i_1, the 10 variable liquids x, y, z etc. besides. We may imagine that these var. liquids are enclosed in spaces with walls, either elastic or not elastic and that the invariant liquids i and i_1 move perpendicularly to the plane of drawing. For the sake of simplicity we shall call a similar system a tissue of cells.

It is easy to deduce now that a stationary state will set in also in these tissues. Then a continuous current of water will flow from i towards i_1 and in such a way that through every cell as much water will flow in as flows out, so that the composition and the quantity of each of the liquids will change no more. From this also follows that [as e.g. is the case in system 12] an equal quantity of water will no longer flow through each membrane.

Omitting the walls of the cells we now shall represent (14) by:

$$\begin{array}{ccccccccccc} u & \rightarrow & v & \rightarrow & w & \rightarrow & m & \rightarrow & p & \rightarrow & q \\ \uparrow & & \uparrow & & \uparrow & & \uparrow & & \downarrow & & \downarrow \\ z & \leftarrow & i & \rightarrow & x & \rightarrow & y & \rightarrow & i_1 & \leftarrow & r \end{array} \quad \ldots\ldots \quad (15)$$

in which the arrows indicate the directions in which the water moves. As however, these directions etc. depend upon the nature and the surfaces of the membranes etc., (15) only represents one of the many cases possible.

It would be possible to determine the partition of the current of the water in (15), if γ_1, γ_2 etc. were known. As, however, these functions are unknown, we shall suppose that the quantity of water, diffusing per second through 1 cM^2 of a membrane, is proportional with the difference of the *O.W.A.*'s of the two adjacent liquids [1]).

Although of course this supposition is quantitatively incorrect, we shall yet use it in order to get some idea of the phenomena.

For the sake of simplicity we shall now assume that the letters in (14) and (15) indicate not only the liquids, but also their *O.W.A.* We shall assume besides that the water diffuses according to the arrows in (15); if this should not be the case, the results will tell us.

We can represent the quantity of water, which liquid x takes in per second from liquid i by:

$$\omega K (x - i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which ω is the surface of the membrane between x and i and K is a constant, determined by the nature of the membrane. As has been assumed in (15) liquid x gives off water to y and w; this quantity is per second:

$$\omega_1 K_1 (y - x) + \omega_2 K_2 (w - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As the quantity of water taken in and given off must be the same, (16) and (17) must be equal to one another. If for the sake of simplicity we now suppose that all membranes have the same surface and the same nature, so that $\omega K = \omega_1 K_1 = \omega_2 K_2$, then follows:

$$x - i = y - x + w - x \text{ or } 3x - y - w = i \quad . \quad . \quad . \quad (18)$$

Acting in a corresponding way for each of the 10 cells, we find the 10 equations (19)

$$\left.\begin{array}{rlrl} 3x - y - w = i & (x) & -x - v + 3w - m = 0 & (w) \\ -x + 3y - m = i_1 & (y) & -y + 3m - p - w = 0 & (m) \\ 2z - u = i & (z) & -m + 3p - q = i_1 & (p) \\ -z - v + 2u = 0 & (u) & -p + 2q - r = 0 & (q) \\ -u + 3v - w = i & (v) & 2r - q = i_1 & (r) \end{array}\right\} . \quad (19)$$

The letters placed between parentheses indicate for which cell an

[1]) For binary liquids we might also take the *W*-amount instead of the *O.W.A.*'s; for liquids with 3 or more substances this is not possible, however. Two liquids L and L', containing the same substances W, X, Y etc. and having the same *W*-amount, will generally yet have a different *O.W.A.* so that also in system $L \mid L'$ water will duffuse.

equation obtains. Solving these equations, we find the 10 relations (20)

$$\left.\begin{array}{lll} 93\,x = 61\,i + 32\,i_1 & 93\,v = 78\,i + 15\,i_1 & 93\,q = 10\,i + 83\,i_1 \\ 93\,y = 32\,i + 61\,i_1 & 93\,w = 58\,i + 35\,i_1 & 93\,r = 5\,i + 88\,i_1 \\ 93\,z = 88\,i + 5\,i_1 & 93\,m = 35\,i + 58\,i_1 & \\ 93\,u = 83\,i + 10\,i_1 & 93\,p = 15\,i + 78\,i_1 & \end{array}\right\} \quad . \quad (20)$$

by which the *O.W.A.* of each of the 10 cells is determined. We see, as was indeed to be expected, that each of these *O.W.A.*'s is greater than i but smaller than i_1. From this it follows:

$$x - i = 32\,(i_1 - i) : 93 \;\; ; \;\; y - x = 29\,(i_1 - i) : 93 \;\; ; \;\; \text{etc.}$$

If everywhere the factor $(i_1 - i) : 93$, occurring in all these results is omitted, we find the 16 relations (21)

$$\left.\begin{array}{llll} x - i = 32 & u - z = 5 & w - x = 3 & i_1 - p = 15 \\ y - x = 29 & v - u = 5 & m - w = 23 & q - p = 5 \\ i_1 - y = 32 & v - i = 15 & m - y = -3 & r - q = 5 \\ z - i = 5 & w - v = 20 & p - m = 20 & i_1 - r = 5 \end{array}\right\} \quad . \quad . \quad (21)$$

The quantity of water diffusing from i towards x or from x towards y per second through 1 cM^2 of the membranes is:

$$\omega\, K\,(x - i) \text{ or } \omega\, K\,(y - x)$$

From this it follows that we may find the quantity of water diffusing per sec. through each of the membranes by multiplying the numbers of (21) with $\omega K\;(i_1 - i) : 93$.

From this it appears that all arrows in (15) indicate the correct direction, except those between m and y; as $m - y$ is negative, the direction must be turned about. Then we get for the scheme of the movement of the water:

$$\begin{array}{ccccccccccc} & 5 & & 20 & & 23 & & 20 & & 5 & \\ u & \rightarrow & v & \rightarrow & w & \rightarrow & m & \rightarrow & p & \rightarrow & q \\ 5\uparrow & & 15\uparrow & & 3\uparrow & & \downarrow 3 & & \downarrow 15 & & \downarrow 5 \\ z & \leftarrow & i & \rightarrow & x & \rightarrow & y & \rightarrow & i_1 & \leftarrow & r \\ & 5 & & 32 & & 29 & & 32 & & 5 & \end{array} \quad . \quad . \quad . \quad (22)$$

The numbers placed with the arrows indicate the ratio of the diffusing quantities of water; [if we suppose these numbers multiplied by $(i_1 - i)\;\omega K : 93$, we have the quantities diffusing per second]. From this it appears that through every membrane does not flow the same quantity of water, that every cell takes in as much water as it gives off and that all the water given off to the tissue by the one invariant liquid, is taken in by the other invariant liquid.

Above we have assumed that all membranes have the same surface (ω) and the same nature (K). Of course every change in a ω or K of one or more of the membranes will also cause a change in the *O.W.A.* of every cell and of the partition of the current of the water. Let us imagine e.g. that between i and v of (14) the membrane becomes less permeable, then K will become smaller for this membrane; if for the sake of simplicity we imagine the membrane impermeable, then its K becomes $= 0$. As cell v will then no longer be in osmotic contact with i but only with u and w, relation (v) of (19) must be replaced now by:

$$v - u = w - v \quad \text{or} \quad -u + 2v - w = 0 \quad . \quad . \quad . \quad . \quad (23)$$

all other relations remain, however.

If x, y etc. are now calculated once more, we find that the *O.W.A.* of each cell and the partition of the current of the water in the tissue have changed. We find this partition in the scheme:

$$\begin{array}{ccccccccccc} & 25 & & 25 & & 43 & & 40 & & 10 & \\ u & \rightarrow & v & \rightarrow & w & \rightarrow & m & \rightarrow & p & \rightarrow & q \\ 25\uparrow & & | & & 18\uparrow & & \downarrow 3 & & \downarrow 30 & & \downarrow 10 \\ z & \leftarrow & i & \rightarrow & x & \rightarrow & y & \rightarrow & i_1 & \leftarrow & r \\ & 25 & & 82 & & 64 & & 67 & & 10 & \end{array} \quad . \quad . \quad . \quad . \quad (24)$$

In order to learn from this the quantities of water diffusing per second, we have to multiply these numbers by $\omega K\,(i_1 - i) : 213$.

We now imagine in (14) the walls between the cells w, m, p and q taken away; we then get a tissue which we represent by

<table>
<tr><td>u</td><td>v</td><td colspan="4">w</td></tr>
<tr><td>z</td><td>i</td><td>x</td><td>y</td><td>i₁</td><td>r</td></tr>
</table>

. . . . (25)

If we now assume the same rules for this again as for (14), we find for the partition of the current of the water the scheme

$$\begin{array}{ccccccccccc} & 32 & & 128 & & & & & & & \\ u & \rightarrow & v & \rightarrow & w & & w & & w & & w \\ 32\uparrow & & 96\uparrow & & 69\uparrow & & 17\downarrow & & 120\downarrow & & \downarrow 60 \\ z & \leftarrow & i & \rightarrow & x & \rightarrow & y & \rightarrow & i_1 & \leftarrow & r \\ & 32 & & 155 & & 86 & & 103 & & 60 & \end{array} \quad . \quad . \quad . \quad (26)$$

In order to learn from this the quantities of water diffusing per second, these numbers must be multiplied by $(i_1 - i)\,\omega K : 344$.

In the osmotic system

$$inv\ i \,|\, inv\ i_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

in which the two invariant liquids are directly in osmotic contact with one another, the quantity of water diffusing per sec. is:

$$(i_1 - i)\,\omega K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Of course this is no longer the case in the tissues discussed above. In (22) $5 + 15 + 32 = 52$ quantities of water are given off by i and taken in by i_1. As, however, these numbers must be multiplied by $(i_1 - i)\,\omega K : 93$ the quantity diffusing per second is:

$$52\,(i_1 - i)\,\omega K : 93 = 0.559\,\omega K\,(i_1 - i) \quad . \quad . \quad . \quad . \quad (29)$$

For the quantity diffusing per second in (24) we find:

$$107\,(i_1 - i)\,\omega K : 213 = 0.502\,\omega K\,(i_1 - i) \quad . \quad . \quad . \quad . \quad (30)$$

and for the tissue (26):

$$283\,(i_1 - i)\,\omega K : 344 = 0.822\,\omega K\,(i_1 - i) \quad . \quad . \quad . \quad . \quad (31)$$

Summarising the preceding considerations, it appears that every change in the surface and the nature of one or more of the membranes and of the position of the cells and invariant liquids with respect to one another, causes:

a change of the *O.W.A.* and consequently also of the composition of the cells;

a change of the partition of the current of the water;

a change of the quantity of water diffusing per second through the tissue.

(To be continued).

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Chemistry. — *The Crystalstructure of Cesium-, Thallium- and Rubidium-Perrhenates.* By F. M. JAEGER and J. BEINTEMA.

(Communicated at the meeting of May 27, 1933).

§ 1. In connection with the determination [1]) of the crystal-structures of the *alkali-osmiamates* of the general formula: $Me^{I}\{Os\,NO_3\}$, it was of interest to extend these investigations to the series of the *alkali-perrhenates*: $Me^{I}\{Re\,O_4\}$, and to compare the two sets of structures with each other. Of these salts, the *potassium-* and *silverperrhenates*

[1]) F. M. JAEGER and J. E. ZANSTRA, these Proceed., **35**, (1932), 610, 787, 779; Recueil d. Trav. d. Chim. d. Pays-Bas, **51**, (1932), 1013—1053.