Chemistry. — *Osmosis in systems containing also liquids with constant compositions.* I. By F. A. H. SCHREINEMAKERS.

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The "up to an invariant liquid path".

In the osmotic system

$$L\,(1) \mid inv.\ L\,(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we suppose there is a membrane, permeable for all substances. On its right side is a liquid 2, the composition of which we suppose constant during the whole of the osmosis; we call this liquid "invariable"; this "invariable", however, applies only to the composition, but not to the quantity of this liquid.

We can keep this liquid practically invariant by continually renewing it during the osmosis at short intervals; we may also cause it to run along the membrane, as happens e.g. with blood in organs and tissues.

This liquid $L\,(2)$, however, may also be really invariant; when it consists of $W + X + Y$, this will be the case e.g. when this liquid is in equilibrium with two more solid substances; e.g. when on the right side of the membrane is found the system:

$$solid\ X + solid\ Y + L\,(2)$$

then the liquid will be saturated with solid X and Y. When water is absorbed, X and Y will dissolve and a new quantity of $L\,(2)$ will form; with emission of water solid X and Y will deposit and a certain quantity of $L\,(2)$ will disappear. When X (or Y) is taken in or given off, only the quantity of solid X (or Y) will increase or decrease.

As during the osmosis liquid $L\,(1)$ changes its composition, we call it "variable"; at the end of the osmosis it gets the same composition as $L\,(2)$.

If in fig. 1 we represent $L\,(1)$ and $L\,(2)$ by the points 1 and 2, then $L\,(1)$ will, during the osmosis, run along a path $1a\,b2$, starting from point 1 and terminating in 2; we call this the "up to invariant $L\,(2)$ path" of the liquid $L\,(1)$. It is clear that $ab\,2$ will then be the up to $L\,(2)$ path of the liquid a, that $b2$ will be that of the liquid b; etc.

If instead of the composition of $L\,(1)$ we keep that of $L\,(2)$ constant, we have the system:

$$inv.\ L\,(1) \mid L\,(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we now leave this system alone, then $L(2)$ will during the osmosis travel along a path $2c\,1$, starting from point 2 and terminating in point 1; it is indeed clear, as will be proved again later on, that this curve must differ greatly from curve $1\,ab\,2$. We now call $2\,c\,1$ the "up to inv. $L(1)$ path" of $L(2)$.

When the systems (1) and (2) have the same membrane, we may consider them as special cases of the system:

$$m_1 \times L(1) \mid m_2 \times L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the membrane is the same as in the systems (1) and (2). On the left side of the membrane now are m_1 quantities of $L(1)$ and on the right side m_2 quantities of $L(2)$. Both liquids now change their compositions till they become equal in a point e (fig. 1) situated on line 1, 2. Then $L(1)$ will travel along branch $1\,e$ and $L(2)$ along branch $2\,e$ of the osmosis-path $1\,e\,2$. Previously [1]) we have seen that the position of point e and consequently also the shape of the osmosis-path depends upon the ratio $m_1 : m_2$; all these curves, however, touch one another in the points 1 and 2.

The greater the quantity m_1 of $L(1)$ becomes ($m_2 =$ constant) the closer e will draw to point 1; then branch $1\,e$ will decrease and branch $2\,e$ increase. When m_1 becomes infinitely large, then e coincides with 1 and only a branch $2\,e = 2\,.\,1$ will remain, along which $L(2)$ travels towards point 1. This branch $2\,e = 2\,.\,1$ is now the same as the up to invariant $L(1)$ path $2\,c\,1$ of liquid $L(2)$. The liquid $L(1)$ of system (3) namely now has become invariant, because we have taken its quantity m_1 infinitely large.

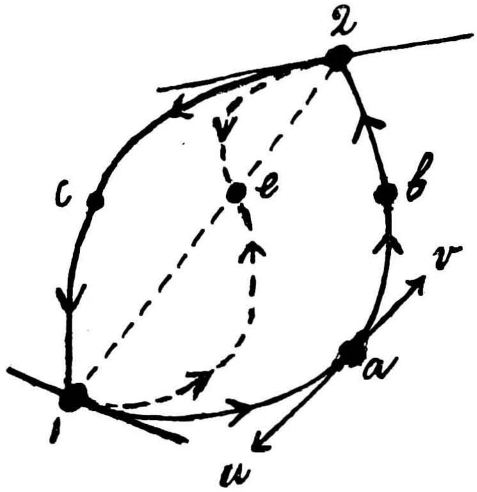

Fig. 1.

In the same way it appears that branch $1\,e$ of the osmosis-path $1\,e\,2$ passes into the up to inv. $L(2)$ path $1\,ab\,2$ of liquid $L(1)$ when in system (3) we take m_2 infinitely large.

From this it follows also that the shape of the up to inv. $L(2)$ path of $L(1)$ in system (1) and of the up to inv. $L(1)$ path of $L(2)$ in system (2) and in general of every up to inv. L path does not depend on the quantity of the variable liquid; the shape of these up paths does depend, however on the nature of the membrane, but, as we shall see later on, it does not depend upon the size of its surface.

[1]) F. A. H. SCHREINEMAKERS. Deze Verslagen **36**, 779, (1927); These Proceedings **30**, 761, (1927).

When, at a certain moment *t*, the left side liquid of system (1) has arrived in point a of path 1 *ab* 2, then system (1) has passed into:

$$L\,(a) \mid inv.\ L\,(2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

At this moment an infinitely small quantity of each of the substances *X*, *Y* and *W* diffuses in the time δt through the membrane in some direction or other. Previously [1]) we have seen that we may also say now: an infinitely small quantity of a mixture, the composition of which we may represent by:

$$x\ mol.\ X + y\ mol.\ Y + (1 - x - y)\ mol.\ W \quad . \; . \; . \quad (5)$$

diffuses. We have called such a mixture, in which x and y may be not only positive and larger than one, but also negative, the "diffusing" mixture.

When x, y and $1 - x - y$ are positive and smaller than 1, then the three substances will go through the membrane in the same direction; then the diffusing mixture is represented by a point of the triangle *WXY*. In the other cases the substances do not go through the membrane in the same direction; then the diffusing mixture is represented by a point, which is situated outside the triangle *W X Y*, viz. in one of the fields II—VII of fig. 1 [2]).

The mixture diffusing in system (4), however, is not situated quite arbitrarily; for we have already deduced previously [3]) that it must be situated somewhere on the line *u a v*, which touches path 1 *ab* 2 in point *a*.

From the direction in which liquid a travels along its up to *L* (2) path, it appears that in the infinitely small time δt it moves an infinitely small distance along the tangent in *a* in the direction from *a* towards *v*. If we imagine the points *u* and *v* of this tangent at an infinite distance, we see:

when the diffusing mixture is situated between *a* and *v*, then the liquid *a* takes in this mixture at this moment of the osmosis;

when the diffusing mixture is situated between *a* and *u*, then the liquid *a* gives off this mixture at this moment of the osmosis.

Now we imagine that point *a* travels along path 1*a b*2; (we shall call the tangent in any position *u a v*); from the above it now follows:

when during the entire osmosis the diffusing mixture is situated between *a* and *v*, then the quantity of the variable liquid will increase continuously;

when during the entire osmosis the diffusing mixture is situated between *a* and *u*, then the quantity of the variable liquid will decrease continuously.

It is possible to imagine that the diffusing mixture will coincide accident-

1) F. A. H. SCHREINEMAKERS. Deze Verslagen, **36**, 1103, (1927); These Proceedings **30**, 1095, (1927).

2) l.c.

3) l.c.

ally with the tangent point at a certain moment of the osmosis. If this should happen e.g. in point b, then in the system:

$$L(b) \mid inv.\ L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

the composition of liquid b would remain constant during the remainder of the osmosis; its quantity, however, changes continuously. When the diffusing mixture goes towards the left, then the quantity $L(b)$ increases continuously; when this mixture goes towards the right, however, then the quantity of $L(b)$ will decrease until at last $L(b)$ has practically been entirely absorbed by the invariant liquid $L(2)$.

In (6) we have a liquid with constant composition on both sides of the membrane; yet there is a great difference between the two liquids. $L(2)$ namely does not change its composition, because we ourselves keep it constant by neutralizing in some way or other the continually occurring changes of concentration; $L(b)$, however, does not change its composition because the diffusing mixture accidentally gets the same composition; so it is a phenomenon which occurs naturally during the osmosis. In order to distinguish these two entirely different cases from one another, we shall call $L(b)$ a "stational" liquid and point b of the path a "stational" point. In order to express this also in (6) we write:

$$stat.\ L(b) \mid inv.\ L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

So the variable liquid $L(1)$ of system (1) now proceeds only along part $1ab$ of path $1a\,b2$; for as soon as it has arrived in the stational point b, it must also remain in this point. Yet this state is far from stable and rather to be called unstable, for any small disturbance, taking this liquid a little farther than this same point b, causes it to travel also along the next part $b2$ of the path. So we shall probably never succeed in realising the stationary state of system (7); it will however be possible to observe that in the vicinity of a stationary point the liquid will change its composition only very slowly.

Of course it will depend upon the nature of the membrane etc. whether a stational liquid can occur or not; later on we shall see that this is always possible in systems with two membranes.

Perhaps we might think that the diffusing mixture cannot pass from one part of the tangent towards the other, without coming into the tangent point, so that a stationary state, such as discussed above, must occur. This is not the case, however.

We imagine this mixture in fig. 1 somewhere on part $a\,v$ of tangent $u\,a\,v$; when it moves away from point a during the osmosis, then it may go through point v towards point u and in this way come on part $u\,a$ of the tangent (the points v and u namely are situated at infinite distance).

At the moment t of this transition, two substances diffuse through the membrane in the one direction and an equal quantity of the third substance in the other direction, as we shall see further on; the total algebraïcal diffusing quantity then is zero. At this moment the liquid does change its composition, but not its quantity; when the quantity had increased before this moment, then it would have decreased afterwards; the quantity of the liquid on the left side of the membrane then passes through a maximum (minimum) at this moment.

We now take the system:

$$inv.\ L(1) \mid inv.\ L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which there is an invariant liquid on both sides; then a constant current of each of the substances X, Y and W goes through the membrane in some direction or other.

If we imagine $L(1)$ variable for a moment, so that it is going to proceed along its path $1\,ab\,2$, then we see that the diffusing mixture must be situated somewhere on the line, touching this path in point 1. If we imagine $L(2)$ variable for a moment, then we see that the mixture must also be situated on the line, touching path $2\,c\,1$ in point 2. The mixture diffusing in system (8) is represented, therefore, by the point of intersection of these tangents. When this point of intersection is situated as in fig. 1 then the mixture is given off by $L(1)$ and taken in by $L(2)$; so in system (8) it will go towards the right. If we assume that this mixture contains e.g. a negative quantity of X and a positive quantity of Y and W [in (5) then: $x < 0, y > 0$ and $1 - x - y > 0$] then the osmosis takes place, therefore, according to the D.T.

$$\longleftarrow X \qquad \longrightarrow Y \qquad \longrightarrow W$$

in which the quantity of $Y + W$ diffusing towards the right, is larger than the quantity of X diffusing towards the left.

In order to illustrate some of the above considerations, we take the system:

$$L(a) \mid inv.\ L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so that the variable liquid is represented by point a of path $1\,ab\,2$. At this moment t in the infinitely short time δt

$$\delta a\ .\ mol.\ X + \delta \beta\ .\ mol.\ Y + \delta \gamma\ .\ mol.\ W \quad . \quad . \quad . \quad . \quad (10)$$

will then diffuse in some direction through the membrane.

For the sake of concentration we take δa positive, when the substance X diffuses towards the left and negative when this passes through the membrane towards the right; we assume the same for $\delta \beta$ and Y and for $\delta \gamma$ and W. We now put:

$$\delta a = x\, \delta m \quad ; \quad \delta \beta = y\, dm \quad ; \quad \delta \gamma = (1 - x - y)\, \delta m \quad . \quad . \quad (11)$$

It now follows from (10) that in the time δt

$$[x \; mol. \; X + y \; mol. \; Y + (1-x-y) \; mol. \; W] \, \delta m \quad . \quad . \quad (12)$$

diffuse. Herein:

$$x \; mol. \; X + y \; mol. \; Y + (1-x-y) \; mol. \; W \quad . \quad . \quad . \quad (13)$$

represents the composition and δm the quantity of the mixture diffusing at this moment in the time δt. It follows from (11) that x, y and δm are completely determined; we find namely

$$\delta m = \delta a + \delta \beta + \delta \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$x = \frac{\delta a}{\delta m} \quad ; \quad y = \frac{\delta \beta}{\delta m} \quad ; \quad 1 - x - y = \frac{\delta \gamma}{\delta m} \quad . \quad . \quad . \quad . \quad (15)$$

As δa, $\delta \beta$ and $\delta \gamma$ may be positive as well as negative, this also obtains for x, y and δm.

We now represent the quantity of the variable liquid a by m_a, its composition by:

$$x_a \; mol. \; X + y_a \; mol. \; Y + (1 - x_a - y_a) \; mol. \; W \quad . \quad . \quad (16)$$

and the change in this composition in the time δt by dx_a and dy_a. As L (a) takes in $\delta a = x \, \delta m$ mol. X and $\delta \beta = y \, \delta m$ mol. Y, we find:

$$dx_a = \frac{m_a \, x_a + x \, \delta m}{m_a + \delta m} - x_a = \frac{x - x_a}{m_a} \, . \, \delta m \quad . \quad . \quad . \quad (17)$$

$$dy_a = \frac{m_a \, y_a + y \, \delta m}{m_a + \delta m} - y_a = \frac{y - y_a}{m_a} \, . \, \delta m \quad . \quad . \quad . \quad . \quad (18)$$

$$\frac{dy_a}{dx_a} = \frac{y - y_a}{x - x_a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

As the first part of (19) determines the direction of the tangent in point a of the path, it follows that the point, representing the composition x, y of the diffusing mixture, must be situated somewhere on tangent $u \, a \, v$. From (19) it appears also that the direction of the tangent and consequently also the form of the path is independent on the quantity m_a of the invariable liquid. It appears from (17) and (18) that m_a, however, does influence dx_a and dy_a and also, therefore, the velocity, with which the variable liquid proceeds along its path.

δm is the quantity of the mixture diffusing in the time δt; this depends upon the surface of the membrane and is proportionate to it. If we take into consideration that δm like m_a does not occur in (19), but occurs in (17) and (18), we see:

the quantity of the variable liquid and the surface of the membrane do not influence the shape of the path; they do, however, influence the velocity of the osmosis and also, therefore, the velocity with which the variable liquid proceeds along its path.

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