Chemistry. — *Osmosis in systems in which also liquids with constant* composition. IV. By F. A. H. SCHREINEMAKERS.

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In the osmotic system

$$L(z) \mid inv.\ L(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is on the left side a variable liquid z and on the right side an invariant liquid i; we assume that the membrane is permeable for all substances (X, Y and W) and that per second:

$$a\ mol\ X + \beta\ mol\ Y + \gamma\ mol\ W \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

run through the membrane. Here we take a positive, when the variable liquid absorbs the substance X, negative when it gives off this substance; we do the same for β and γ with respect to the substances Y and W.

We represent the composition of the invariant liquid i by:

$$x\ mol\ X + y\ mol\ Y + (1-x-y)\ mol\ W \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and that of the variable liquid z by:

$$(x+\xi)\ mol\ X + (y+\eta)\ mol\ Y + (1-x-\xi-y-\eta)\ mol\ W \quad . \quad . \quad (4)$$

so that we have x and y as constants and ξ and η as variables.

When n quantities of the variable liquid z are present at a certain moment t, then at the moment $t + dt$ there are:

$$n + (a+\beta+\gamma)\ dt = n + \mu dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

quantities. The n quantities of this liquid contain $n\ (x+\xi)$ mol. X, the $n + \mu\ dt$ quantities contain $n\ (x+\xi) + a\ dt$ mol X, having been absorbed $a\ dt$ mol. X. From this it follows that the change $d\xi$ in the X-amount of this liquid in the time dt is:

$$d\xi = \frac{n\ (x+\xi) + adt}{n+\mu dt} - (x+\xi) = \frac{a - (x+\xi)\ \mu}{n + \mu dt}\ dt \quad . \quad . \quad . \quad (6)$$

In a corresponding way we find for the change $d\eta$ in the Y-amount:

$$d\eta = \frac{\beta - (y+\eta)\ \mu}{n+\mu dt} \, . \, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It now follows from (6) and (7):

$$\frac{d\eta}{d\xi} = \frac{\beta - (y+\eta)\ \mu}{a - (x+\xi)\ \mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

by which the tangent in every point of the path of the variable liquid z has been determined.

The quantity of X, diffusing through the membrane per second in system (1), depends upon the composition of the two liquids z and i and on the nature of the membrane ; so we have :

$$\alpha = \varphi(x+\xi, y+\eta, x, y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which function of course also contains the magnitudes determining the nature of the membrane. Although this function is not known, we yet know that for $\xi = 0$ and $\eta = 0$ we shall also have $\alpha = 0$.

When the composition of the variable liquid z differs only very little from that of the invariant liquid, so that ξ and η are very small, then we may write for (9):

$$\alpha = A\xi + A'\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which A and A' would be known, if we knew the function φ ; however it is clear that A and A' both are functions of x and y and of the magnitudes, determining the nature of the membrane.

In a corresponding way we find :

$$\beta = B\xi + B'\eta \quad \text{and} \quad \gamma = C\xi + C'\eta \quad . \quad . \quad . \quad . \quad . \quad (11)$$

As we have put $\alpha + \beta + \gamma = \mu$, as appears from (5), follows :

$$\mu = D\xi + D'\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which $D = A + B + C$ and $D' = A' + B' + C'$.

Above we have seen that the tangent in every point of the path of the variable liquid z is determined by (8); if we now imagine this liquid in the immediate vicinity of point i, so that ξ and η are very small, then α, β and μ will be very small also ; at first approximation we may, therefore, neglect $\xi\mu$ and $\eta\mu$; then (8) passes into :

$$\frac{d\eta}{d\xi} = \frac{\beta - y\mu}{\alpha - x\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If here we substitute the values of α, β and μ from (10), (11) and (12) then we find :

$$\frac{d\eta}{d\xi} = \frac{(B-yD)\,\xi + (B'-yD')\,\eta}{(A-xD)\,\xi + (A'-xD')\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

by which the direction of the tangent to the path has been determined in the immediate vicinity of point i. For the sake of simplicity we now write for (14) :

$$\frac{d\eta}{d\xi} = \frac{m\xi + n\eta}{p\xi + q\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

in which the values of m, n, p and q follow from (14).

When we leave the osmotic system (1) to itself, then at the end of the osmosis the variable liquid z will get the same composition as the invariant liquid i; the path of the variable liquid ends, therefore, in point i. From this follows for small values of ξ and η:

$$\frac{\eta}{\xi}=\frac{d\eta}{d\xi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

If we substitute this value of $\eta : \xi$ in (15), then follows:

$$q\left(\frac{d\eta}{d\xi}\right)^2+(p-n)\frac{d\eta}{d\xi}-m=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As the path of the variable liquid ends in point i, $\frac{\delta\eta}{\delta\xi}$ must have a real value; so equation (17) must have two real roots, which we shall call u_1 and u_2. Then we have:

$$\frac{d\eta}{d\xi}=u_1 \quad \text{and} \quad \frac{d\eta}{d\xi}=u_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

for which we may write also, as follows from (16):

$$\eta-u_1\,\xi=0 \quad \text{and} \quad \eta-u_2\,\xi=0 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From this it appears, as has also been discussed already in Comm. III, that all paths meeting in point i, have only two tangents, which we have called the axes of the bundle; the direction of these axes is determined by the roots u_1 and u_2 of equation (17); from this it appears that the direction of these axes depends upon m, n, p and q and consequently on the place of point i and the nature of the membrane.

From this, however, it does not yet follow that these two axes also have the property, discussed in Comm. III, namely:

an infinite number of paths touches one of the axes (the principal axis); only two paths or in special cases only one touches the other axis (secondary axis).

In order to deduce this and also in order to learn the shape of the paths in the vicinity of point i, we shall integrate (15). If we put:

$$\frac{\eta}{\xi}=u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

then follows from (15):

$$u+\xi\frac{du}{d\xi}=\frac{m+nu}{p+qu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

from which follows after conversion:

$$\frac{d\xi}{\xi}+\frac{qu+p}{qu^2+(p-n)\,u-m}\,du=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

If we imagine in (17) $\frac{\delta\eta}{\delta\xi}$ substituted by u, we get the equation :

$$qu^2 + (p-n)\,u - m = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

which must have two real roots u_1 and u_2, as we have seen for (17). So for (22) we may write also :

$$\frac{d\xi}{\xi} + \frac{qu+p}{q\,(u-u_1)\,(u-u_2)}\,du = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If in the well-known way we divide the coefficient of du into two fractions, (24) passes into :

$$q\,(u_1-u_2)\frac{d\xi}{\xi} + (qu_1+p)\frac{du}{u-u_1} - (qu_2+p)\frac{du}{u-u_2} = 0 \quad . \quad . \quad (25)$$

By integration follows :

$$\xi^{q(u_1-u_2)} \times (u-u_1)^{qu_1+p} = K\,(u-u_2)^{qu_2+p} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

in which K is an arbitrary constant. If we here substitute for u its value of (20) then we find after conversion :

$$(\eta-u_1\,\xi)^{qu_1+p} = K\,(\eta-u_2\,\xi)^{qu_2+p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

As we may give K any arbitrary value, (27) represents therefore, an infinite number of paths, viz. all the paths, meeting in point i.

As in deducing (15) we have assumed, however, that ξ and η are very small (27) also will obtain only for small values of ξ and η ; so (27) only determines the paths of the bundle in the vicinity of point i and not at a greater distance.

With the aid of the properties of the roots of equation (23) we find :

$$(qu_1+p)\,(qu_2+p) = np - mq \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

So the two exponents in (27) have the same sign when $np > mq$ and opposite signs when $np < mq$. So we may distinguish two cases with respect to the sign of these exponents; we shall see, however, that only one of these cases is of real significance for us.

1. When $np > mq$ the two exponents in (27) have the same sign. For the sake of concentration we shall now assume that the absolute value of $qu_1 + p$ is smaller than that of $qu_2 + p$. We now write (27):

$$\eta - u_1\xi = K\,(\eta - u_2\xi)^{\frac{qu_2+p}{qu_1+p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so that the exponent of the second part is positive now and greater than 1. Equation (29) represents a bundle of paths, touching the straight line

$$\eta - u_1\xi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

in point i; we imagine this line represented by line KiK' in fig. 2 of Comm. III. All these paths, as follows from (29), are parabolically curved in the vicinity of point i; their curvature depends upon the value of K and is consequently different for all paths.

In the special case that we put $K=0$, (29) passes into (30); then in the vicinity of point i the path will be a straight line, coinciding in fig. 2 of Comm. III either with iK or with iK'; consequently there are two paths here, having this property.

In the special case that we put $K=\infty$ (or when we substitute K by $1:K$ and then put $K=0$) (29) passes into:

$$\eta - u_2\xi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

We imagine this straight line represented by hih' in fig. 2 of Comm. III. Consequently there are now two paths fi and $f'i$ which are straight lines in the vicinity of point i and coincide with hi and $h'i$.

From this it follows in accordance with what we have already deduced above in (18) and (19) from (17), that all paths have only two tangents in point i. At the same time it now appears, however, and this did not follow from (17), namely that an infinite number of paths now touch the line $\eta - u_1\xi = 0$ and that only two paths touch the line $\eta - u_2\xi = 0$. Consequently the principal axis of the bundle has been defined by the root u_1 and the additional axis by the root u_2 of equation (23).

Above we have assumed that the absolute value of $qu_1 + p$ is smaller than that of $qu_2 + p$; when the reverse is the case, then the principal axis is determined by the root u_2 and the additional axis by the root u_1.

2. When $np < mq$ both exponents in (27) have opposite signs; then we may write for this:

$$(\eta - u_1\xi)^a\,(\eta - u_2\xi)^b = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

in which a and b are positive. We now take first the special case that $K=0$; then we may satisfy (32) by:

$$\eta - u_1\xi = 0 \quad \text{and} \quad \eta - u_2\xi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

If we imagine these lines represented again by KiK' and hih' in fig. 2 of Comm. III, then there must be two paths, coinciding in the vicinity of point i with line KiK' and two paths, coinciding with hih' in the vicinity of this point.

If, however, we give to K a value, other than zero, then (32) can never be satisfied by $\xi = 0$ and $\eta = 0$. From this it appears that (32) represents a bundle of curves, all of which (except the four, determined by $K=0$) do not end in point i. As, however, every path of a variable liquid must end in point i the curves, defined by (33), cannot represent osmosis-paths.

Reversally we now may also conclude that the coefficients of m, n, p

and q in (15) or in (23) cannot satisfy $np < mq$, but that, as we have assumed sub 1, we must have $np > mq$.

Although the curves, determined by (32) do not represent osmosis-paths, I yet wish, in connection with later considerations, to point out the fact that they are hyperbolical curves, having the lines (33) as asymptotes.

When a variable liquid z is found at a moment t in a point z of its path, then, as we have seen already in Comm. I, the composition of the mixture diffusing in the time dt will be represented by a point z_0, situated on the tangent, that may be drawn to the path in point z.

When towards the end of the osmosis the liquid z comes in the immediate vicinity of point i, the tangent in this point will coincide either with the principal or with the secondary axis of the bundle; the mixture z_0 diffusing at this moment, must, therefore also be situated either on the principal axis or on the secondary axis.

When this mixture z_0 is situated on the principal axis, then it may be situated as well on part iK as on iK' (fig. 2 Comm. III). When z_0 is situated on iK, then all variable liquids, the paths of which touch iK, will give off this mixture towards the end of the osmosis; all variable liquids, the paths of which touch iK', will absorb this mixture towards the end of the osmosis.

When the mixture z_0 is situated on the secondary axis, then it may be situated either on ih or on ih'. When z_0 is situated on ih, the variable liquid proceeding along path fi, will give off this mixture towards the end of the osmosis; the variable liquid, proceeding along path $h'i$, will absorb this mixture.

So towards the end of the osmosis there are only two diffusing mixtures, one of which is situated on the principal axis, the other on the secondary axis. The first obtains for an infinitely great number of paths, viz. for all the paths touching the principal axis; the latter obtains only for the two paths, accidentally touching the secondary axis and can, therefore, occur only under very special conditions.

It appears from these considerations that not only the position of both the axes of a bundle, but also the composition of the mixture z_0, diffusing towards the end of the osmosis, depends upon the composition of the invariant liquid and on the nature of the membrane.

Till now we have assumed that the roots u_1 and u_2 of equation (23) are different; when, however, this equation has two equal roots u_0 we find that all paths in the vicinity of point i touch the line $\eta - u_0\,\xi = 0$; then the bundle has one single axis only.

We may also imagine the very special case that equation (23) has an infinite number of roots, viz. that any arbitrary value of u will satisfy (23). This is the case when accidentally

$$q = 0, \quad n = p \quad \text{and} \quad m = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

have been satisfied. Instead of (15) and (27) we then get:

$$\frac{d\eta}{d\xi}=\frac{\eta}{\xi} \quad \text{and} \quad \eta=K\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

In this special case all paths now are straight lines in the vicinity of point i, meeting from all directions in point i; we now might say that the bundle of point i has an infinite number of axes. Later on we shall refer to some special cases.

(To be continued.)

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