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

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In Comm. IV we have seen: when there is still only a very small difference (ξ and η) between the variable liquid z of the osmotic system:

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

and the composition (x and y) of the invariant liquid i, we can represent α, β and γ (viz. the quantities of X, Y and W, diffusing per second) and the total quantity μ ($\mu = \alpha + \beta + \gamma$) by:

$$\left.\begin{array}{ll} \alpha = A\,\xi + A'\eta & \beta = B\,\xi + B'\eta \\ \gamma = C\,\xi + C'\eta & \mu = \mu\,\xi + \mu'\eta \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The path along which the variable liquid proceeds, is then determined in the vicinity of the invariant point i by:

$$\frac{d\eta}{d\xi} = \frac{m\,\xi + n\,\eta}{p\,\xi + q\,\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

in which:

$$m = B - y\,D; \quad n = B' - y\,D'; \quad p = A - x\,D; \quad q = A' - x\,D' \qquad (4)$$

All paths of the bundle are determined then in the vicinity of point i by:

$$(\eta - u_1\,\xi)^{qu_1+p} = K\,(\eta - u_2\,\xi)^{qu_2+p} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

in which u_1 and u_2 are the roots of the equation:

$$q\,u^2 + (p - n)\,u - m = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

This bundle has two axes, the direction of which is determined by u_1 and u_2; an infinite number of paths touches the principal axis, only two paths touch the secondary axis. We now shall discuss some special cases.

1. First we take the osmotic system:

$$L(z) \mid inv.\, (water) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

in which the invariant liquid consists of pure water only, so that it is represented in fig. 5 (Comm. III) by point W; so we now have to put in (4) $x = 0$ and $y = 0$.

We now begin by supposing the variable liquid z in a point r on side WX; then we have $\eta = 0$ while ξ has a positive value. We now imagine

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this point r in the immediate vicinity of W so that β (viz. the diffusing quantity of Y) is now defined by $\beta = B\xi$, as follows from (2). As, however, the two liquids contain water and X only, so that no Y can diffuse, β must be $=0$; from this follows $B=0$.

If we imagine the variable liquid in a point s on side WY so that no X can diffuse now, we find in a corresponding way $A'=0$.

In the special case that the invariant liquid consists of water only we have, therefore:

$$x=0; \quad y=0; \quad A'=0; \quad B=0 \quad \ldots\ldots \quad (8)$$

It now follows from (4):

$$m=0; \quad n=B'; \quad p=A; \quad q=0 \quad \ldots\ldots \quad (9)$$

Instead of (3) we now have:

$$\frac{d\eta}{d\xi}=\frac{n}{p}\cdot\frac{\eta}{\xi} \quad \ldots\ldots\ldots\ldots \quad (10)$$

in which n and p are determined by (9). From this follows:

$$\eta^p = K\,\xi^n \quad \ldots\ldots\ldots\ldots \quad (11)$$

in which, as we have seen previously, the two exponents must have the same sign. It now follows from (11) that the lines $\eta=0$ and $\xi=0$ (viz. the sides WX and WY) are the axes of this bundle. We now can distinguish three cases

a. $\frac{p}{n}>1$. Now we write (11) in the form:

$$\eta^{\frac{p}{n}} = K\,\xi. \quad \ldots\ldots\ldots\ldots \quad (12)$$

so that the exponent of η is greater than 1. Then all paths are parabolical in the vicinity of point W and touch the line $\xi=0$ viz. side WY, as has been drawn in fig. 5 (Comm. III). This appears besides among other things also in the following way; from (12) namely follows:

$$\frac{p}{n}\cdot\frac{d\eta}{d\xi}=K:\eta^{\frac{p}{n}-1} \quad \ldots\ldots\ldots\ldots \quad (13)$$

As the exponent of η is positive here, it follows that $\frac{\delta\eta}{\delta\xi}$ becomes infinitely large for small values of η; so the paths touch WY, as has been said already before. Consequently this side WY is the principal axis of the bundle, whereas WX is the secondary axis.

In this special case there is no path touching the secondary axis, but this secondary axis WX is a path itself.

b. $\frac{p}{n} < 1$. Now we write (11) in the form:

$$n = K\,\xi^{\frac{n}{p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that now the exponent of ξ is greater than 1. We now find that all paths touch the line $\eta = 0$ viz. side WX. Now side WX is the principal axis and WY the secondary axis.

c. $\frac{p}{n} = 1$. In this very special case, which will occur only accidentally and which represents the transition from *a* towards *b*, (11) passes into:

$$\eta = K\,\xi \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In this very special case all paths now are in the vicinity of point W straight lines, meeting in point W.

Before we have seen that the shape of the paths in the vicinity of the invariant point W is determined by the value of $p/_{n}$. In order to deduce this value we suppose the variable liquid z in point r of fig. 5 (Comm. III); when this point is situated in the immediate vicinity of W, the diffusing quantity of X is determined by $\alpha = A\xi$. From (9) now also follows $\alpha = p\xi$.

If we imagine the variable liquid in point r, we find $\beta = B'\eta = n\eta$.

If we now put $\xi = \eta$ viz. the X-amount of the liquid r equal to the Y-amount of the liquid s, then follows:

$$\frac{p}{n} = \frac{\alpha}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

We now may say: when $\alpha > \beta$ viz. when towards the end of the osmosis X diffuses more quickly than Y, then all paths touch the Y-axis; when $\alpha < \beta$ viz. when the substance X diffuses more slowly than Y, then all paths touch the X-axis; in the transition-case $\alpha = \beta$ viz. when the two substances diffuse with the same rapidity, then all paths are straight lines, meeting from all directions in point W.

2. We now take the osmotic system:

$$L(z) \mid inv.\, L(i_2)\,[water + Y] \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which the invariant liquid consists of water and the substance Y only; we imagine this liquid represented in fig. 4 (Comm. III) by point i_2.

If we now suppose the variable liquid on side WY in the vicinity of point i_2, we find in a similar way as in 1. that A' must be $= 0$. As in point i_2 $x = 0$ also, it follows from (4) $q = 0$ also. Equation (3) now passes into:

$$\frac{d\eta}{d\xi} = \frac{m\,\xi + n\,\eta}{p\,\xi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If here we put $\eta = u\,\xi$, we find after conversion:

$$\frac{d\xi}{\xi} + \frac{p\,du}{(n-p)\,u + m} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

from which we find by integration:

$$\xi = K\,[(n-p)\,u + m]^{\frac{p}{n-p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

If here we again put $u = \eta : \xi$, we find:

$$\xi = K\,[(n-p)\,\eta + m\,\xi]^{\frac{p}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

by which the paths of the bundle in the vicinity of point i_2 are defined. From (21) it follows that line $\xi = 0$ (viz. side WY) and the line:

$$(n-p)\,\eta + m\,\xi + 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

which has been indicated in fig. 4 (Comm. III) by $i_2\,h$, are the axes of this bundle.

Of course it depends again upon the value of $\frac{p}{n}$ which of these two axes is the principal axis and which the secondary axis; if we take $\frac{p}{n} > 1$, then it follows from (21) that an infinite number of paths touches line $\xi = 0$; line $i_2\,h$ then is touched by one path only, which has been represented in fig. 4 by fi_2. Then side WY is the principal axis and line $i_2\,h$ the secondary axis of this bundle.

3. In the osmotic system:

$$L\,(z) \mid inv.\ L\,(i_1)\,[water + X] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

the invariable liquid consists of water and X only; we imagine this liquid represented in fig. 4 (Comm. III) by point i_1.

We now find $B = 0$ and because in point i_1 also $y = 0$, it now follows from (4) : $m = 0$. Equation (3) now passes into:

$$\frac{d\eta}{d\xi} = \frac{n\,\eta}{p\,\xi + q\,\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If we again put $\eta = u\,\xi$ here. we find after conversion:

$$(p-n)\,\frac{d\xi}{\xi} + q\,\frac{du}{u} - n\,q\,\frac{du}{su + r - n} = 0 \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If we integrate this equation and if we then again put $u = \eta : \xi$, we find:

$$\eta^{\frac{p}{n}}\,K\,[q\,\eta + (p-n)\,\xi] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

by which the paths of the bundle are determined in the vicinity of point i_1. From this it follows that line $\eta = 0$ (viz. side WX) and line:

$$q\eta + (p-n)\xi = 0 \quad \ldots \ldots \ldots \quad (27)$$

which has been indicated by $i_1 k$ in fig. 4 (Comm. III), are the axes of this bundle.

Here again it will depend once more upon the value of $\frac{p}{n}$ which of these axes is the principal axis and which the secondary axis. If we again take $\frac{p}{n} > 1$, then it follows from (26) that an infinite number of paths touches the line, determined by (27); so the line $i_1 k$ is the principal axis of the bundle and the side WX the secondary axis. In this special case there is no path touching the secondary axis; this secondary axis WX, however, consists of the two straight-lineal paths Wi_1 and Xi_1.

We now take the osmotic system:

$$inv.\, L(i_1) \underset{\omega_1}{\overset{M_1}{\Big|}} L(z) \underset{\omega_2}{\overset{M_2}{\Big|}} inv.\; L(i_2) \quad \ldots \ldots \quad (28)$$

in which a variable liquid z between the two invariant liquids i_1 and i_2. During the osmosis, in which the substances W, X and Y will run through the two membranes with different velocities and in different directions, the variable liquid z changes its composition, until at last a stationary state sets in, which we represent by:

$$inv.\; L(i_1) \underset{\omega_1}{\overset{M_1}{\Big|}} stat.\; L(u) \underset{\omega_2}{\overset{M_2}{\Big|}} inv.\; L(i_2) \quad \ldots \ldots \quad (29)$$

As we have seen in the Comm. II and III, the osmosis is not done in this state, but W, X and Y will go on diffusing continuously through the two membranes; then, however, the stationary liquid u does not change its composition any more, but it does change its quantity.

We now represent the composition of the variable liquid z at a moment t by:

$$x'\, mol\, X + y'\, mol\;\; Y + (1 - x' - y')\, mol\, W \quad \ldots \quad (30)$$

and its quantity by n. If as in the preceding Comm. we now represent the quantity, taken in per second by the variable liquid, by:

$$\alpha\, mol\, X + \beta\, mol\, Y + \gamma\, mol\, W \quad \ldots \ldots \quad (31)$$

then the changes dx' and dy' of its X- and Y-amount and the change dn of its quantity in the time dt, are determined by:

$$dx' = \frac{\alpha - x'\mu}{n} . \,dt; \quad dy' = \frac{\beta - y'\mu}{n} dt; \quad dn = \mu\, dt \quad \ldots \quad (32)$$

in which, just as previously, $\mu = \alpha + \beta + \gamma$. It appears from (32) that the variable liquid does not change its composition any more, when

$$\alpha - x'\mu = 0 \quad \text{and} \quad \beta - y'\mu = 0 \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Then the osmotic system (28) has passed into the stationary state (29).

We can also find (33) easily in the following way. When namely the composition of the variable liquid z does not change any more, then α, β and γ (viz. the quantities of X, Y and W, taken in or given off) must be proportionate to the concentrations x', y' and 1-x'-y' of the liquid z; then we must have:

$$\frac{\alpha}{x'} = \frac{\beta}{y'} = \frac{\gamma}{1 - x' - y'} = \frac{\alpha + \beta + \gamma}{1} = \frac{\mu}{1} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

in which the 4th and 5th term follow at once from the three first terms. With the aid of the first and the last term and the second and the last term we find (33) at once.

In order to define these results more precisely, we imagine that per second in system (28)

$$\alpha_1 \, mol \, X + \beta_1 \, mol \, Y + \gamma_1 \, mol \, W \quad . \quad . \quad . \quad . \quad . \quad (35)$$

diffuse through 1 cM^2 of the membrane M_1 towards the left, namely from the variable liquid z towards the invariant liquid i_1. [So in (35) α_1 is positive, when the substance X runs towards the left and negative when this substance runs towards the right; the same obtains for β_1 and γ_1].

Further we imagine that in (28) per second:

$$\alpha_2 \, mol \, X + \beta_2 \, mol \, Y + \gamma_2 \, mol \, W \quad . \quad . \quad . \quad . \quad . \quad (36)$$

diffuse towards the left through 1 cM^2 of the membrane. If we represent the surfaces of the two membranes by ω_1 and ω_2, then we have, therefore:

$$\left.\begin{array}{ll} \alpha = -\omega_1 \alpha_1 + \omega_2 \alpha_2 & \beta = -\omega_1 \beta_1 + \omega_2 \beta_2 \\ \gamma = -\omega_1 \gamma_1 + \omega_2 \gamma_2 & \mu = -\omega_1 \mu_1 + \omega_2 \mu_2 \end{array}\right\} \quad . \quad . \quad . \quad (37)$$

If we now represent the composition of the stationary liquid u by x and y, so that in (33) we must put $x' = x$ and $y' = y$, then follows from (33) and (37):

$$\left.\begin{array}{ll} x = \dfrac{-\omega_1 \alpha_1 + \omega_2 \alpha_2}{-\omega_1 \mu_1 + \omega_2 \mu_2} & y = \dfrac{-\omega_1 \beta_1 + \omega_2 \beta_2}{-\omega_1 \mu_1 + \omega_2 \mu_2} \end{array}\right\} \quad . \quad . \quad . \quad (38)$$

by which, as we shall see further on, the composition of the stationary liquid u has been determined.

The quantities α_1 and α_2 [viz. the quantities of X, diffusing towards the left in system (28) per second through 1 cM^2 of the membrane M_1 and M_2] are determined by:

$$\alpha_1 = \varphi_1 (x' \, y') \quad \text{and} \quad \alpha_2 = \varphi_2 (x' \, y') \quad . \quad . \quad . \quad . \quad . \quad (39)$$

in which x' and y' indicate the composition of the variable liquid z. The function φ, however, contains besides the composition of the invariant liquid i_1 and the magnitudes, determining the nature of the membrane. The same obtains for φ_2 with respect to the invariant liquid i_2 and the membrane M_2.

Of course corresponding functions obtain for β_1, β_2, γ_1 and γ_2. When the variable liquid z of system (28) passes into the stationary liquid u of (29), then in (39) we must put $x'=x$ and $y'=y$. We now see that we may write the two equations (38) in the form:

$$F_1(x\,y)=\frac{\omega_1}{\omega_2} \quad \text{and} \quad F_2(x\,y)=\frac{\omega_1}{\omega_2} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

so that x and y and the ratio $\omega_1:\omega_2$ must satisfy two equations. From this it appears that the composition (xy) of the stationary liquid u depends upon:

a. the composition of the two invariant liquids i_1 and i_2.

b. the nature of the two membranes and the ratio of their surfaces.

So with every definite ratio $\omega_1:\omega_2$ the stationary liquid u has a definite composition, which is determined by (40).

We now imagine the invariant liquids i_1 and i_2 and the stationai liquid u of the systems (28) and (29) in fig. 1 (Comm. II) represented by the points 1, 2 and u. If we now imagine a variable liquid in the point a (b, c or d), then this proceeds along the path au (bu, cu or du); so we have a bundle of paths, all meeting and terminating in point u. The direction of the tangent to an arbitrary point of a path, is determined by:

$$\frac{dy'}{dx'}=\frac{\beta-y'\mu}{\alpha-x'\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

as follows from (32).

If we now imagine the variable liquid z in the vicinity of the stationary point u, then we may put:

$$x'=x+\xi \quad \text{and} \quad y'=y+\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

in which ξ and η are very small. Instead of (41) we then may write:

$$\frac{d\eta}{d\xi}=\frac{\beta-(y+\eta)\,\mu}{\alpha-(x+\xi)\,\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

When x' and y' approach x and y, then as the osmosis in the stationary point still continues all the time, $\alpha_1=\varphi_1(x'\,y')$ and $\alpha_2=\varphi_2(x'\,y')$ will not approach zero, but definite values, which we shall call $\alpha_{1.0}$ and $\alpha_{2.0}$. For small values of ξ and η we then have:

$$\left.\begin{aligned}&\alpha_1=\alpha_{1.0}+A_1\,\xi+A'_1\,\eta\,; \quad \alpha_2=\alpha_{2.0}+A_2\,\xi+A'_2\,\eta\\&\alpha=-\,\omega_1\,\alpha_{1.0}+\omega_2\,\alpha_{2.0}+(-\,\omega_1\,A_1+\omega_2\,A_2)\,\xi+(-\,\omega_1\,A'_1+\omega_2\,A'_2)\,\eta\end{aligned}\right\} \quad (44)$$

In a corresponding way we have:

$$\left.\begin{aligned}\beta &= -\omega_1 \beta_{1.0} + \omega_2 \beta_{2.0} + (-\omega_1 B_1 + \omega_2 B_2)\xi + (-\omega_1 B'_1 + \omega_2 B'_2)\eta \\ \mu &= -\omega_1 \mu_{1.0} + \omega_2 \mu_{2.0} + (-\omega_1 D_1 + \omega_2 D_2)\xi + (-\omega_1 D'_1 + \omega_2 D'_2)\eta\end{aligned}\right\} \quad (45)$$

If we substitute these values in (43) and if we take into consideration that all magnitudes with the index 0 (viz. $\alpha_{1.0}$, $\alpha_{2.0}$ etc.) now must satisfy (38), we find:

$$\frac{d\eta}{d\xi} = \frac{m\xi + n\eta}{p\xi + q\eta} \quad \ldots \ldots \ldots \quad (46)$$

in which terms of higher order have been omitted. Herein is:

$$\left.\begin{aligned}m &= -\omega_1 (B_1 - yD_1) + \omega_2 (B_2 - yD_2) \\ n &= -\omega_1 (B'_1 - yD'_1) + \omega_2 (B'_2 - yD'_2) - \mu \\ p &= -\omega_1 (A_1 - xD_1) + \omega_2 (A_2 - xD_2) - \mu \\ q &= -\omega_1 (A'_1 - xD'_1) + \omega_2 (A'_2 - xD'_2)\end{aligned}\right\} \quad \ldots \quad (47)$$

in which μ represents the total quantity:

$$\mu = -\omega_1 \mu_{1.0} + \omega_2 \mu_{2.0} \quad \ldots \ldots \ldots \quad (48)$$

per second taken in or given off by the stationary liquid u.

In a corresponding way as in Comm. IV it now appears from (46) that the bundle of all paths, meeting in a stationary point, has two axes; namely a principal axis, touched by an infinite number of paths, and a secondary axis, touched only by two paths. The position of these axes depends upon:

a. the composition of the two invariant liquids i_1 and i_2.

b. the nature of the two membranes and the ratio of their surfaces.

Although, as appears from (47), n and p contain the term μ, the position of the axes of the bundle is yet dependent on μ. The position namely is determined by the roots of equation (6), which contains, however, only the difference p—n, so that in this equation μ does not occur; so the term μ will only influence the shape of the paths at some distance from the stationary point.

In an other discussion of experimental determinations in some of these systems and in considerations on membranes, I shall refer to this once more.

(To be continued.)

Leiden, *Lab. of Inorg. Chemistry.*