Chemistry. — *Membrane and Osmosis IV.* By F. A. H. SCHREINEMAKERS.

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Osmosis of binary liquids through a membrane M(n).

We now consider an osmotic system

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

in which L and L' are binary liquids; we imagine them represented by two points on the line WX of figs. 1—4 M.O.I. For the sake of concentration we shall suppose the liquid L to be always on the left side of L' in these figures. As membrane *M(n)* is permeable for all substances, we may imagine the four D.T.'s (Diffusion-Types) of scheme I and the four transition-D.T.'s of scheme II.

Scheme I				Scheme II		
	W	X			W	X
a.	$\longleftarrow 0$	$\longleftarrow$	(*cond.*)	*e.*	———	$\longleftarrow$
b.	$\longrightarrow$	$\longleftarrow$		*f.*	$\longrightarrow$	———
c.	$\longrightarrow$	$\longrightarrow 0$	(*cond.*)	*g.*	$[\text{———}$	$\longrightarrow 0]$
d.	$[\longleftarrow 0$	$\longrightarrow 0]$		*h.*	$[\longleftarrow 0$	$\text{———}\ ]$

Previously [1]) we have deduced:

in an osmotic system with a membrane *M(n)* all D.T.'s are possible, except the incongruent one.

In order to determine the incongruent D.T. we must therefore begin by knowing the incongruent direction of the water and of the substance X in system (1). Previously we have said:

the congruent direction of a substance is the direction in which it travels through a membrane, permeable for this substance only; the incongruent direction is the opposite one.

In order to determine the congruent direction of the water, we have to replace the membrane *M(n)* in system (1) by a membrane *M(W)*; we then have:

$$L \mid M(W) \mid L' \longrightarrow W \quad \ldots\ldots\ldots \quad (2)$$

in which the water diffuses according to the direction of the arrow;

1) F. A. H. SCHREINEMAKERS. Verslagen Kon. Akad. v. Wet. Amsterdam, **37** 634 (1928); These Proceedings, **31** 811 (1928).

this follows at once from our discussions in M.O. III, e.g. from *F*, *G* or *H*.

In order to determine the congruent direction of the substance X we take the system.

$$L \mid M(X) \mid L' \longleftarrow X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now we find that the substance diffuses towards the left.

We now know the congruent directions of W and X in (2) and (3); we now see that the arrows, beside which the sign 0 has been placed in schemes I and II, indicate an incongruent direction; so *b* is the congruent and *d* the incongruent D.T.; *a* and *c* are mixed D.T's. From this follows:

in system (1) the three D.T.'s *a*, *b* and *c* and the two transition-D.T.'s *e* and *f* are possible; the D.T.'s placed between parentheses, are not possible.

We now suppose the compositions of the liquids L and L' of system (1) kept constant in some way or other, so that a stationary current of W and X travels through the membrane.

We now represent the quantities of W and X, diffusing in a definite time and through a definite part of the surface of a membrane according to the congruent D.T. (viz. *b*) by w_b and x_b.

The more the membrane now approaches a membrane $M(X)$ and the quantity of W, which diffuses, consequently decreases, the more $w_b : x_b$ will approach zero.

The more the membrane approaches a membrane $M(W)$ and the diffusing quantity of X consequently decreases, the more $w_b : x_b$ will approach ∞; so we find:

A) in the congruent D.T. the ratio between the diffusing quantities of W and X can have all values between 0 and ∞.

This does not obtain any longer, however, in the mixed D.T.'s *a* and *c*. We imagine a membrane, for which the D.T. *a* obtains; we shall call it a membrane $M(a)$. We assume that w_a quantities of W and x_a quantities of X diffuse through it; we shall represent this diffusion by:

$$M(a) \qquad \longleftarrow 0 \; w_a \; mol. \; W \qquad \longleftarrow x_a \; mol. \; X. \quad . \quad . \quad (4)$$

We now imagine also a membrane $M(c)$ for which the D.T. *c* obtains; we represent this diffusion by:

$$M(c) \qquad \longrightarrow w_c \; mol. \; W \qquad \longrightarrow 0 \; x_c \; mol. \; X \; . \quad . \quad (5)$$

We now imagine these membranes $M(a)$ and $M(c)$ between the liquids L and L' at the same time; then through the one membrane W and X will run towards the left and through the other towards the right.

We now regulate the surfaces of these membranes in such a way, that in the same period of time as much water will go through $M(c)$ towards the right as through $M(a)$ towards the left. We can do this by taking the surface of the membrane $M(c)$ $w_a : w_c$ times larger; then the diffusion through the membrane $M(c)$ will become:

$$M\,(c) \qquad \longrightarrow w_a \textit{ mol. } W \qquad \longrightarrow 0 \, \frac{w_a}{w_c} \, . \, x_c \textit{ mol. } X. \quad (6)$$

If the diffusions according to (4) and (6) now take place at the same time, the W-quantity of both liquids will not change; the quantity of X, however, does change; for now we still have the diffusion:

$$\longrightarrow 0 \left(\frac{w_a}{w_c} \, . \, x_c - x_a \right) \textit{ mol. } X \; . \; . \; . \; . \; . \; . \quad (7)$$

We now distinguish three cases:

1) $\frac{w_a}{w_c} x_c > x_a$. Now a part of the substance X will diffuse towards the right, viz. incongruently. If we now put in still an other membrane $M(X)$, then by regulating its surface, we can arrange that the same quantity of X runs towards both sides. As we then have a system, in which the liquids change neither their compositions nor their quantities, we should get eternal circular currents of W and X; we assume however that this is not possible.

2) $\frac{w_a}{w_c} x_c = x_a$. Now the same quantity of W and the same quantity of X runs in both directions; then we also have continuous circular currents of W and X.

3) $\frac{w_a}{w_c} x_c < x_a$. The substance X now runs in congruent direction; as we cannot neutralize this current by an other membrane, both liquids will change; so at last a state of equilibrium will arise, so that the X-current disappears also.

From this follows that only case 3 can be possible, viz.

$$\frac{w_a}{w_c} < \frac{x_a}{x_c} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

So we may say:

B) in each of the mixed D.T.'s the ratio of the diffusing quantities of W and X can have an infinite number of values; these values, however, must always be smaller in D.T. a than in D.T. c.

We may further elucidate the previous considerations with the aid of the O.W. A. and the O. X. A. of the liquids. For this purpose we suppose an osmotic system:

$$\left. \begin{array}{ccc} & L \mid M\,(n) \mid L' & \\ \longleftarrow \alpha \textit{ mol. } X & & \longleftarrow \gamma \textit{ mol. } W \end{array} \right\} \; . \; . \; . \; . \quad (9)$$

in which α mol. X and γ mol. W diffuse towards the left. When α and

γ are very small, then, as we have seen before[1]), they have to satisfy:

$$\alpha\,[\xi_x - \xi'_x] + \gamma\,[\xi_w - \xi'_w] > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in wich ξ_x and ξ'_x represent the O. X. A., and ξ_w and ξ'_w the O.W. A. of the liquids L and L'. We now represent the X-amount of these liquids by x and x' (consequently their W-amount by $1-x$ and $1-x'$). As we shall see later on we now can prove that α and γ must satisfy:

$$\alpha\,[1-(x)] - \gamma\,(x) > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in wich (x) has a definite value, which is situated between x and x'. If we take $x < x'$, as we have always supposed it to be until now, then we consequently have:

$$x < (x) < x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

We now begin by supposing a membrane $M(W)$ in system (9), so that no X diffuses; then we have the system (2), discussed already before. As now $\alpha = 0$, γ must satisfy:

$$-\gamma\,(x) > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

as follows from (11); therefore γ must be negative. This means, as it appears from (9) that the water must diffuse towards the right. This is in accordance with the arrow in system (2).

If in (9) we imagine a membrane $M(X)$, we get system (3). As now $\gamma = 0$, it follows from (11) that α must be positive. (9) shows that X must now diffuse towards the left; this is also in accordance with the arrow in system (3).

In accordance with previous discussions it appears from this that in scheme I *b* is the congruent D.T., *d* the incongruent and *a* and *c* are the mixed D.T.'s.

(11) can always be satisfied by pos. values of α and neg. values of γ; it appears from (9) that the diffusion then takes place according to the D.T.:

$$\longrightarrow W \qquad \longleftarrow X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

viz. the congruent D.T. of scheme I; what has been said in A above, also follows from it.

If we were to take $\gamma =$ pos. and $\alpha =$ neg., we should have the incongruent D.T.:

$$\longleftarrow 0\,W \qquad \longrightarrow 0\,X \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This is not possible, however, because the first part of (11) for $\gamma =$ pos. and $\alpha =$ neg. is always negative.

We can also satisfy (11) by pos. values of γ and α-; then we have the mixed D. T. a of scheme I. We now cannot take α and γ arbitrarily, however; for, as appears from (11) they must satisfy:

$$\frac{\gamma}{\alpha} < \frac{1-(x)}{(x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

[1]) F. A. H. SCHREINEMAKERS, l. c.

From this it appears that in the D.T. *a* the ratio of the diffusing quantities of W and X must always be smaller than the value of the second part of (16).

(11) can also be satisfied by negative values of α and γ; we then have the mixed D.T.*c*. If we put $\alpha = -\alpha'$ and $\gamma = -\gamma'$ so that α' and γ' are positive, then we find from (11) that they have to satisfy:

$$\frac{\gamma'}{\alpha'} > \frac{1-(x)}{(x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

So in the D.T. *c* the ratio of the diffusing quantities of W and X must always be greater than the value of the second part of (17).

Consequently from (16) and (17) follows not only what has already been said above in B, but besides that the limit of these ratios is determined by the second part of (16) and of (17).

We now suppose the liquids L and L' represented once more by two points of the line WX (figs. 1—4 M.O. I); the liquid L (as has been frequently stated before) is always situated on the left side of L'.

In the D.T. *b* the liquid L gives off water and takes in X; both reasons cause the X-amount of L to increase; consequently L travels along line WX towards the right.

As liquid L takes in water and gives out X, its W-amount will consequently decrease of these two reasons; so L' moves towards the left.

We may represent this by:

$$D.T.\,b \qquad \longrightarrow L \qquad \longleftarrow L' \quad . \quad . \quad . \quad . \quad . \quad (18)$$

in which the arrows indicate the direction in which the liquids travel along line WX.

In the mixed D.T. *a*, however, we may distinguish two cases, namely:

$$D.T.\,\mathrm{a} \qquad \longrightarrow L \qquad \longleftarrow L' \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$D.T.\,\mathrm{a} \qquad \longrightarrow L \qquad \longrightarrow L' \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The liquid L namely absorbs water and X; now we may say that liquid L absorbs a liquid L_0; this liquid L_0 contains:

$$\alpha \text{ mol. } X + \gamma \text{ mol. } W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The liquid L' now gives out this liquid L_0. As α and γ are both positive, we now may also write for (11):

$$\frac{\alpha}{\alpha+\gamma} > (x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

in which the first part is the X-amount of the liquid L_0. If we represent the X-amount of L and L' by x and x', then it follows from the signification of (x):

$$x < (x) < x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

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This shows that α and γ will most certainly satisfy:

$$\frac{\alpha}{\alpha+\gamma} > x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

in which the second part is still smaller than in (22). This means: the diffusing liquid L_0 has a larger X-amount than L. As, therefore, L absorbs a liquid with a larger X-amount, L will consequently shift towards the right.

If in (22) we substitute (x) by the larger value x', then the first part may be larger as well as smaller than the second; so we have:

$$\frac{\alpha}{\alpha+\gamma} \gtreqless x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

This means: the diffusing liquid L_0 may have a greater as well as a smaller and also a similar X-amount as the liquid L'.

From this it appears that the liquid L' may travel as well towards the left as towards the right and may also happen to remain unchanged.

With the osmosis according to the mixed D.T. c we may distinguish two corresponding cases, which the reader will be able to deduce easily; then the liquid L' will always shift towards the left.

Above we have seen that α and γ in system (9) have to satisfy (10). Here, as we have seen formerly: [1])

$$\xi_x = -\zeta - (1-x)\frac{\partial \zeta}{\partial x} \quad ; \quad \xi_w = -\zeta + x\frac{\partial \zeta}{\partial x} \quad . \quad . \quad . \quad . \quad (26)$$

We now have:

$$\xi'_x = \xi_x + \int_x^{x'} d\xi_x \qquad \xi'_w = \xi_w + \int_x^{x'} d\xi_w \quad . \quad . \quad . \quad . \quad (27)$$

From (26) follows:

$$d\xi_x = -(1-x)\, r\, dx \qquad d\xi_w = xr\, dx \quad . \quad . \quad . \quad . \quad (28)$$

in which the meaning of r follows from the deduction. If we substitute these values in (27), we find:

$$\xi_x - \xi'_x = \int_x^{x'} (1-x)\, r\, dx = \int_x^{x'} r\, dx - \int_x^{x'} xr\, dx \quad . \quad . \quad . \quad (29)$$

$$\xi_w - \xi'_w = -\int_x^{x'} xr\, dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

[1]) l. c.

As $x' > x$ and r is always positive, these integrals are positive also. It is easy to see now that we may put:

$$\int_{x}^{x'} xr\,dx = (x) \int_{x}^{x'} r\,dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

in which (x) has a definite value between x and x'. If we substitute this in (29) and (30), we get:

$$\xi_x - \xi'_x = [1 - (x)] \int_{x}^{x'} r\,dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\xi_w - \xi'_w = -(x) \int_{x}^{x'} r\,dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

If we substitute this value in (10) and if we divide by the integral, we find (11).

We now imagine a system

$$\left.\begin{array}{c} n \times L \mid M(n) \mid n' \times L' \\ \longleftarrow \triangle a \ mol.\ X \qquad \longleftarrow \triangle \gamma \ mol.\ W \end{array}\right\} \quad . \quad . \quad . \quad . \quad (34)$$

in which $\triangle a$ *mol.* X and $\triangle \gamma$ *mol.* W diffuse towards the left. We then get the system:

$$(n + \triangle a + \triangle \gamma) \times L_1 \mid M(n) \mid (n' - \triangle a - \triangle \gamma) \times L'_1 \quad . \quad . \quad (35)$$

in which L_1 and L'_1 represent the new liquids. The first system has a thermodynamical potential $n\zeta + n'\zeta'$; that of the second system is

$$(n + \triangle a + \triangle \gamma)\, \zeta_1 + (n' - \triangle a - \triangle \gamma)\, \zeta'_1$$

If we now put $\triangle a + \triangle \gamma = \triangle s$ then, as the thermodynamical potential may decrease only, we must have:

$$(n + \triangle s)\, \zeta_1 + (n' - \triangle s)\, \zeta'_1 - n\zeta - n'\zeta' < 0 \quad . \quad . \quad . \quad (36)$$

We represent the increase of the X-amount of the left-side liquid by $\triangle x$; we then have:

$$\triangle x = \frac{nx + \triangle a}{n + \triangle a + \triangle \gamma} - x = \frac{\triangle a - x \triangle s}{n + \triangle s} \quad . \quad . \quad . \quad . \quad (37)$$

If we represent the increase of the X-amount of the right-side liquid by $\triangle x'$, then we have:

$$\triangle x' = \frac{n'x' - \triangle a}{n' - \triangle a - \triangle \gamma} - x' = \frac{-\triangle a + x' \triangle s}{n' - \triangle s} \quad . \quad . \quad (38)$$

Now we write (36) in the form:

$$(n+\triangle s)(\zeta_1-\zeta)+(n'-\triangle s)(\zeta_1'-\zeta')+\triangle s\,.\,(\zeta-\zeta')<0 \quad . \quad (39)$$

If we substitute herein the values of $n+\triangle s$ and $n'-\triangle s$, which follow from (37) and (38), then (39) passes into:

$$(\triangle a-x\triangle s)\frac{\zeta_1-\zeta}{\triangle x}-(\triangle a-x'\triangle s)\frac{\zeta_1'-\zeta'}{\triangle x'}+\triangle s(\zeta-\zeta')<0. \quad (40)$$

We now suppose the ζ-curve of the liquids, consisting of W and X, drawn in an x, ζ-diagram. We imagine a line through the two points, representing the thermodynamical potentials of the two left-side liquids L and L_1 (systems 34 and 35); we call this line the left-side chord. As the coordinates of the one point are x and ζ and those of the other point $x+\triangle x$ and ζ_1, so for the coordinates Z and X of this chord obtain:

$$Z=\zeta+\frac{\zeta_1-\zeta}{\triangle x}(X-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Now we also imagine a line through the two points, representing the thermodynamical potentials of the two right-side liquids L' and L'_1 (systems 34 and 35). For this right-side chord now obtains:

$$Z=\zeta'+\frac{\zeta_1'-\zeta'}{\triangle x'}(X-x') \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

These left-side and right-side chords intersect one another in a point; if we represent the X of this point by (x), then this satisfies:

$$\zeta+\frac{\zeta_1-\zeta}{\triangle x}[(x)-x]=\zeta'+\frac{\zeta_1'-\zeta'}{\triangle x'}[(x)-x'] \quad . \quad . \quad . \quad (43)$$

We now write (42) in the form:

$$[(x)-x]\frac{\zeta_1-\zeta}{\triangle x}-[(x)-x']\frac{\zeta_1'-\zeta'}{\triangle x'}+(\zeta-\zeta')=0 \quad . \quad . \quad (44)$$

We now multiply (43) by $\triangle s$ and then subtract this from (40); we then get:

$$[\triangle a-(x)\triangle s]\frac{\zeta_1-\zeta}{\triangle x}-[\triangle a-(x)\triangle s]\frac{\zeta_1'-\zeta'}{\triangle x'}<0 \quad . \quad . \quad (45)$$

or:

$$[\triangle a-(x)\triangle s]\left[\frac{\zeta_1-\zeta}{\triangle x}-\frac{\zeta_1'-\zeta'}{\triangle x'}\right]<0 \quad . \quad . \quad . \quad . \quad (46)$$

We now have:

$$\frac{\zeta_1-\zeta}{\triangle x}<\frac{\zeta_1'-\zeta'}{\triangle x'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

The left-side form namely is the tangens of the angle, which the left-side chord makes with the X-axis; the right-side form is the tangens of the angle, which the right-side chord makes with the X-axis. In a system in which no unmixing can occur and in which, therefore, every liquid is stable with respect to all other liquids, the tangens of this right-side angle is always greater than the tangens of the left-side angle. We see this at once when we keep in mind that the ζ-curve is convex in all points. As the second factor of (45) is, therefore, negative, the first must be positive; from this follows:

$$\triangle \alpha - (x) \triangle s > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

If we here put $\triangle s = \triangle \alpha + \triangle \beta$ again, then (47) passes into:

$$\triangle \alpha \,.\, [1 - (x)] - \triangle \gamma \, (x) > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Above we have seen that (x) is determined by the point of intersection of the left-side and right-side chords in ihe x, ζ-diagram. If we imagine (x) represented by a point on the line WX, then we see that the left-side liquids L and L_1 are situated on the left side of (x) and the right-side liquids L' and L'_1 on the right side. From this follows:

$$x \text{ and } x + \triangle x < (x) < x' \text{ and } x' + \triangle x' \quad . \quad . \quad . \quad . \quad (50)$$

It appears from the deduction that $\triangle \alpha$ and $\triangle \gamma$ may be finitely as well as infinitely small; if we take both infinitely small and if we put $\triangle \alpha = \alpha$ and $\triangle \gamma = \gamma$, then (48) passes into (11). As $\triangle x$ and $\triangle x'$ are now infinitely small also, the left-side and the right-side chords will pass into tangents to the ζ-curve; then (x) is determined by the point of intersection of the left-side and right-side tangents; so in (11) (x) has an other value than in (48).

We shall further refer to (48) later on.

(*To be continued*).

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