Chemistry. — Osmosis of ternary liquids. General considerations. VI. By F. A. H. SCHREINEMAKERS.

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Congruent, incongruent osmosis and the membrane.

We now consider the osmotic system:

We represent the composition of the liquid L by:

 $x \mod X + y \mod Y + (1 - x - y) \mod W$ 

and that of the liquid L' by:

$$x' \mod X + y' \mod Y + (1 - x' - y') \mod W$$

We now cause a small quantity of the substances X, Y and W (viz. a,  $\beta$  and  $\gamma$  mol) to diffuse in the direction of the arrows, consequently from right to left.

The *n* quantities of *L* first contain *nx* mol. *X* and *ny* mol. *Y*; afterwards there are on the left side of the membrane  $n + a + \beta + \gamma$  quantities of liquid, containing nx + a mol. *X* and  $ny + \beta$  mol. *Y*. The composition of *L* has changed, therefore, with:

$$dx = \frac{nx + a}{n + a + \beta + \gamma} - x = \frac{(1 - x)a - x\beta - x\gamma}{n + a + \beta + \gamma}$$
$$dy = \frac{ny + \beta}{n + a + \beta + \gamma} - y = \frac{-ya + (1 - y)\beta - y\gamma}{n + a + \beta + \gamma}$$
$$(2)$$

We may find the changes dx' and dy' of the right side liquid L' by giving the opposite sign to  $\alpha$ ,  $\beta$  and  $\gamma$  in (2).

If we represent the Th. d. pot. (thermodynamical potential) of the liquid L by Z, then, its composition changing with dx and dy, this will become:

As there are now  $n + a + \beta + \gamma$  quantities of this liquid on the left side, the Th. d. pot. on the left side of the membrane will increase with:

$$(n+a+\beta+\gamma)\left(Z+\frac{\partial Z}{\partial x}dx+\frac{\partial Z}{\partial y}dy\right)-nZ$$
 . (4)

Substituting dx and dy of (2) here, we shall find:

Here:

$$\xi_{x} = -Z - (1 - x) \frac{\partial Z}{\partial x} + y \frac{\partial Z}{\partial y}$$
  

$$\xi_{y} = -Z + x \frac{\partial Z}{\partial x} - (1 - y) \frac{\partial Z}{\partial y}$$
  

$$\xi_{w} = -Z + x \frac{\partial Z}{\partial x} + y \frac{\partial Z}{\partial y}$$
  
(6)

to the meaning of which we shall refer later on.

If we represent the Th. d. pot. of liquid L' by Z', then we find in a corresponding way that the Th. d. pot. on the right side of the membrane increases with:

$$\xi'_x \alpha + \xi'_y \beta + \xi'_w \gamma \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

We find  $\xi'_x \xi'_y$  and  $\xi'_w$  by giving to all variables in (6) the sign '. Consequently, as follows from (5) and (7), the Th. d. pot. of the total system increases with:

As this total Th. d. pot. cannot do anything but decrease or remain constant, so (8) must be either negative or zero. Consequently  $\alpha$ ,  $\beta$  and  $\gamma$  may not be taken arbitrarily, but they have to satisfy the condition:

In (3) we have neglected the higher powers of dx and dy; if we limit ourselves to terms of the second order, we must still add the term:

$$q = \frac{1}{2} (r \, dx^2 + 2 \, s \, dx \, dy + t \, dy^2)$$

to (3) and consequently a term nq to (5). In the same way it appears that we must still add a term n'q' to (7) and, therefore, still a term N = nq + n'q' to (8). We are able to compute q and q' and, consequently also N; for our purpose, however, it is not necessary. For our purpose it is sufficient to know the sign of N and, if we consider stable liquids only, this is positive, because q and q' then are positive. Instead of (9) a,  $\beta$  and  $\gamma$  must, therefore, satisfy:

$$(\xi_x - \xi'_x) \alpha + (\xi_y - \xi'_y) \beta + (\xi_w - \xi'_w) \gamma - N \ge 0$$
 . . (10)

in which N is a term of the second order, which is positive for all values of  $\alpha$ ,  $\beta$  and  $\gamma$ .

Now we shall first take the simple case that only one of the substances e.g. W (water) passes through the membrane; then  $\alpha$  and  $\beta$  are zero and system (1) passes into the system:

$$n \times L \mid n' \times L' \longleftarrow \gamma . W . . . . . (11)$$

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Instead of (10) we now get:

$$(\xi_w - \xi'_w) \gamma - C \gamma^2 \ge 0$$
 . . . . . . (12)

in which C is positive. We now distinguish 3 cases.

1.  $\xi_w > \xi'_w$ . As  $\gamma^2$  is infinitely small with respect to  $\gamma$ , the sign of (12) is defined by the first term; consequently  $\gamma$  must satisfy:

As the coefficient of  $\gamma$  is positive,  $\gamma$  must be positive also. Therefore, in (11) the water diffuses in the direction of the arrow, viz. towards the left.

2.  $\xi_w < \xi'_w$ . We now see that  $\gamma$  must be negative; now the water diffuses in (11) in a direction opposite to that of the arrow, viz. towards the right.

3.  $\xi_w = \xi'_w$ . Instead of (12) we now have:

As C is positive and  $\gamma^2$  is also positive for all values of  $\gamma$ , the first part of (14) must always be negative; consequently we can only satisfy (14) by  $\gamma = 0$ . So no W passes through the membrane and the two liquids are in osmotic equilibrium.

We see from this that it depends on the values of  $\xi_w$  en  $\xi'_w$  (viz. on their difference) whether water will diffuse and in what direction it will go. Now we call  $\xi_w$  the O.W.A. (osmotic water-attraction) of the left side liquid and  $\xi'_w$  the O.W.A. of the right side liquid. If we represent a membrane, through which only W diffuses, by M(W), then we may say, therefore:

water diffuses through a membrane M(W) towards that side, where the O.W.A. is the greatest;

if both liquids have the same O.W.A., then no water passes through a membrane M(W).

We now take a liquid g, represented in fig. 1 by point g. We now may put the question: are there any other liquids, which have the same O.W.A. as this liquid g? We then have to satisfy:

$$(\xi_w)_g = -Z + x \frac{\partial Z}{\partial x} + y \frac{\partial Z}{\partial y}$$
 . . . . . (15)

The left part represents the O.W.A. of the liquid g and has, therefore, a definite value. The right part represents (comp. 6) the O.W.A. of the liquid looked for. As its composition (xy) must satisfy (15), it follows: there exists an infinite number of liquids, which have the same O.W.A. as liquid g; they are all situated on a curve ab (fig. 1) going through point g; previously we have called it the isotonic *W*-curve.

Although the liquids of this isotonic curve may have a very different amount of W, they yet have the same O.W.A. In the systems:

$$L_f \mid L_g$$
;  $L_g \mid L_h$ ;  $L_a \mid L_b$ . . . . (16)

etc., therefore, no water will diffuse through the membrane M(W).

It is clear that there exists an infinite number of isotonic curves; in fig. 1 three of them have been drawn, viz.  $a_1b_1$ , ab and  $a_2b_2$ . All liquids



of  $a_1b_1$ , therefore, have the same O.W.A., also those of ab and those of  $a_2b_2$ . As we shall see directly, the O.W.A. of the liquids of curve ab, however, is greater than that of curve  $a_1b_1$ , and that of curve  $a_2b_2$ greater again than that of curve ab. Among others these curves have the following properties.

1. Two isotonic curves can never intersect or touch one another.

2. Every straight line, going through point W, intersects an isotonic curve in one point only.

3. The O.W.A. of the liquids of an isotonic curve becomes greater, the farther this curve is situated from point W.

4. The isotonic curves are straight lines in the vicinity of point W; farther away they are curved and may get all kind of forms.

For the O.W.A. of a liquid is valid:

$$\xi_w = -Z + x \frac{\partial Z}{\partial x} + y \frac{\partial Z}{\partial y}.$$

From this follows:

$$d\xi_w = (xr + ys) dx + (xs + yt) dy$$
 . . . . (17)

If *n* quantities of liquid take in  $\delta n$  quantities of *W*, then dx and dy are defined by (2), in which we then have to put a = 0,  $\beta = 0$  and  $\gamma = \delta n$ . We then find for (17):

$$d\xi_w = -(rx^2 + 2s xy + ty^2) \frac{\delta n}{n}$$
. . . . . (18)

As the form, placed between parentheses, is positive, it follows from this: the O.W.A. of a liquid decreases when it takes in water  $(\delta n \text{ pos.})$ ; the O.W.A. increases, when it gives off water  $(\delta n \text{ neg.})$ .

When in fig. 1 a liquid passes along line lW (viz. starting from l towards W) then its W-amount increases continuously; consequently its O.W.A. decreases; if, however, it passes along line Wl (viz. from W to l) then its O.W.A. increases.

From this we can immediately deduce the properties 1-3, mentioned above.

If we take liquid c of curve  $a_1 b_1$  (fig. 1) and liquid q of curve  $a_2 b_2$ , we have the system:

$$L_c \mid L_q \longrightarrow W$$
 . . . . . . (19)

in which the right side liquid has a larger O.W.A. than the left side one; consequently through a membrane M(W) water diffuses towards the right. Therefore, liquid c gives off water and moves along line clin the direction of the arrow in point c; its O.W.A. increases. The liquid q takes in water and moves along line qW in the direction of the arrow in point q; its O.W.A. increases. The diffusion of water will continue till both liquids get the same O.W.A., consequently till they reach the same isotonic W-curve. If we assume that this is on curve ab, then, at the end of the osmosis liquid c comes in g and liquid q in *i*. Consequently system (19) passes into the osmotic equilibrium:

$$L_g \mid L_i \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (20)$$

in which no W diffuses anymore <sup>1</sup>).

All that has been deduced above for the substance W (water), obtains also for every arbitrary other substance.

If e.g. only the substance X passes through the membrane, then system (1) passes into:

$$n \times L \mid n' \times L' \longleftarrow a \cdot X \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (21)$$

(10) now passes into:

$$(\xi_x - \xi'_x) \alpha - A \alpha^2 \ge 0$$
 . . . . . . (22)

In the same way as described above, it follows from this that it depends on the values of  $\xi_x$  and  $\xi'_x$  whether the substance X will diffuse

<sup>&</sup>lt;sup>1</sup>) For positive, negative, normal and anormal osmosis in those systems, compare : F. A. H. SCHREINEMAKERS, Osmosis of liquids. The Journal of General Physiology. Vol. 11, N<sup>0</sup>, 6, pp. 701-713 (1928).

and in what direction it will go. We shall call  $\xi_x$  and  $\xi'_x$  the O.X.A. (osmotic X-attraction) of the liquids.

It appears in the same way that it depends on  $\xi_y$  and  $\xi'_y$  whether the substance Y will diffuse and in which direction it will go; we shall call this the O.Y.A. of the liquids.

If we take an arbitrary substance S and a membrane M(S), viz. a membrane which only lets through this substance S, then we may say, therefore:

substance S diffuses through a membrane M(S) towards that side, where the O.S.A. is greatest;

if both liquids have the same O. S. A., then no S passes through a membrane M(S);

there exists an infinite number of liquids, which have the same O.S.A. as a given liquid.

In fig. 2 we find three curves, passing through point 1. Curve ab is an isotonic W-curve; it represents the liquids which have the same O.W.A. as liquid 1. Curve cd is an isotonic X-curve; it represents the



liquids, which have the same O. X. A. as liquid 1. Curve ef is an isotonic Y-curve; it represents the liquids which have the same O.Y.A. as liquid 1.

Above we have seen that there exists an infinite number of isotonic W-curves; consequently there exists an infinite number of isotonic X-and Y-curves. Of course the same properties as have been discussed above for the W-curves, obtain also for them. Therefore, we find among other things:

the O.X.A. (O.Y.A.) of the liquids of an isotonic X-curve (Y-curve) is greater the further those curves are away from point X(Y).

When the three dotted curves also represent isotonic curves, then we have, therefore:

the liquids of curve ab have a smaller O.W.A. than those of curve a'b';

the liquids of curve cd have a greater O. X. A. than those of curve c'd';

the liquids of curve ef have a smaller O. Y. A. than thos of curve e'f'.

Among other things it follows from the above that liquid 1 has a greater O.X.A., but a smaller O.Y.A. and O.W.A. than liquid p. We represent this by:

$$\underbrace{\begin{array}{cccc} L_1 \mid L_p & \text{fig. 2} \\ O. X. A. & O. Y. A. & O. W. A. \\ \longleftarrow & \longrightarrow & \longrightarrow \end{array}} \right\} \quad . \quad . \quad (23)$$

in which, therefore, the arrows point towards that side of the membrane. where the osmotic attraction is greatest. Consequently those arrows also indicate the direction in which a substance diffuses through a membrane, which transmits this substance only.

Consequently X diffuses through a membrane M(X) towards the left, Y through a membrane M(Y) and W through a membrane M(W) towards the right.

We now take the liquids 1 and q of fig. 2. If we imagine the three isotonic curves also drawn through q, then we see that liquid 1 has a larger O. X. A. and a larger O. W. A., but a smaller O. Y. A. than liquid q. We represent this by:

Consequently we see that X diffuses through a membrane M(X) and W through a membrane M(W) towards the left and Y through a membrane M(Y) towards the right.

For the liquids 1 and r we find:

For the liquids 1 and s obtains:

For the liquids 1 and t we find:

and for the liquids 1 and u:

We shall call those systems (23)—(28) the systems  $p, q \dots u$ .

We now take a system:

in which a membrane M(XYW) or M(3) viz. a membrane which transmits the three substances. Then the question arises:

in which direction will each of the substances X, Y and W now go through the membrane?

We shall begin by assuming that every substance can diffuse as well towards the left as towards the right; then we can distinguish the eight cases of scheme I (we are shortly going to refer to the letters p, q etc. placed between parentheses). We call each of those cases a D. T. ("diffusion-type").

In order to simplify a further discussion, we shall call the direction, in which X diffuses through a membrane M(X) (consequently from a smaller towards a greater O.X.A.) the "congruent" direction of X. We call the opposite direction (consequently from a greater towards a smaller O.X.A.) "incongruent". We act in the same way with Y, W and other substances.

We now call a diffusion-type:

"congruent" when all substances diffuse congruently;

"incongruent" when all substances diffuse incongruently.

"mixed" when at the same time congruent and incongruent directions occur.

We shall first consider the system p (viz. 23). As in (23) the arrows indicate the side, where the osmotic attraction is greatest, they indicate the congruent direction of each of the substances X, Y and W. If we compare these directions with those of scheme I, we see:

N<sup>0</sup>. 4 represents the congruent and N<sup>0</sup>. 5 the incongruent D. T. of system p.

In order to indicate that N<sup>0</sup>. 5 is the "incongruent" D.T. of system p, the letter p has been put here between parentheses.

If in scheme I we imagine the sign o to be placed on the right side of each arrow, indicating an incongruent direction, we get scheme Ip.



This shows quite clearly that N<sup>0</sup>. 4 is the congruent and N<sup>0</sup>. 5, placed between parentheses, the incongruent D.T. of system q. The other D.T. are mixed; in 2, 3 and 8 one substance goes incongruently through the membrane, in 1, 6 and 7 two substances.

In system q (viz. 24) the arrows also indicate the congruent directions of the substances X, Y and W; consequently N<sup>0</sup>. 3 of scheme I represents the congruent D. T. of this system and N<sup>0</sup>. 6 the incongruent D. T. This has again been indicated scheme I by placing the letter qbetween parentheses with N<sup>0</sup>. 6. For this system q we now find the scheme I q.

If we only pay attention to the fact whether a system goes through the membrane towards the left or towards the right, the D.T. of scheme Ipare the same as those of Iq. If, however, we also take into consideration the "congruentness" or "incongruentness" of these directions, then there is a great difference.

For instance in N<sup>0</sup>. 1 of Ip substances do go through the membrane in the same direction as in N<sup>0</sup>. 1 of Iq; but in the first case Y and W diffuse incongruently and in the second Y only.

For the other D. T. we find corresponding differences.

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In a corresponding way we find the congruent and consequently also the incongruent D. T. of the other systems. In (30) we find them united for all systems.

system
 
$$p$$
 $q$ 
 $r$ 
 $s$ 
 $t$ 
 $u$ 

 congr.
  $D.T.$ 
 4
 3
 7
 5
 6
 2

 incongr.
  $D.T.$ 
 5
 6
 2
 4
 3
 7

We also see this in scheme I; the letter r, placed between parentheses with N<sup>0</sup>. 2, namely indicates that N<sup>0</sup>. 2 is the incongruent D. T. of system r, etc. In the same way as this has been done above for the systems p and q, the reader also may deduce a scheme for each of the other systems and indicate the incongruent directions in it by the sign 0.

From scheme I or (30) appears among other things:

the composition of the two liquids determines which of the 8 D. T. is congruent (incongruent);

all D. T. can be congruent (incongruent) except 1 and 8.

So for each osmotic system, having a membrane M(3), eight different D. T. exist; we must, however, put the question whether they all are possible.

For this purpose we take system (1), in wich a mol. X,  $\beta$  mol. Y and  $\gamma$  mol. W diffuse towards the left. When a is negative, X goes in the opposite direction, when  $\beta$  is negative, Y goes in the opposite direction, and when  $\gamma$  is negative, W goes in the opposite direction. If we pay attention to the signs, which we can give to  $\alpha$ ,  $\beta$  and  $\gamma$ , we get the eight D.T. of scheme I.

We have already seen, however, that  $\alpha$ ,  $\beta$  and  $\gamma$  can not be taken quite arbitrarily, but have to satisfy (10). In this we put:

$$\xi_x - \xi'_x = K_x$$
;  $\xi_y - \xi'_y = K_y$ ;  $\xi_w - \xi'_w = K_w$ . (31)

As long as the three first terms together do not amount to zero, the sign of (10) will be determined by these terms. If we put, therefore:

$$K = aK_x + \beta K_y + \gamma K_w \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

then  $\alpha$ ,  $\beta$  and  $\gamma$  must satisfy:

$$K > 0$$
 . . . . . . . . . . . . (33)

When the three terms of K are positive, then, (33) has consequently been satisfied; when one or two terms are negative,  $\alpha$ ,  $\beta$  and  $\gamma$  may yet be chosen either so large or so small that K will be positive; when each of the three terms is negative, however, K is always negative. Consequently we are not able to satisfy (33) when at the same time:

$$\alpha K_x < 0$$
 ;  $\beta K_y < 0$  ;  $\gamma K_w < 0$  . . . . (34)

When  $aK_x$  is negative, then a and  $K_x$  must have opposite signs. If we consider the value of  $K_x$  in (31), we can distinguish two cases.

1.  $\xi_x > \xi'_x$  and a < 0. Consequently the O.W.A. is larger on the left side of the membrane than on the right side; therefore, the congruent direction of X is towards the left; [consequently through a membrane  $M(\lambda)$ , X would go towards the left]. As, however, a now is negative, X diffuses towards the right, i.e. incongruently.

2.  $\xi_x < \xi'_x$  and a > 0. Now the congruent direction of X is towards the right. As, however, a is positive now, X diffuses towards the left, consequently once more incongruently.

 $aK_x < 0$  means, therefore, that the substance X diffuses incongruently;  $\beta K_y < 0$  and  $\gamma K_w < 0$  have the same meaning for Y and W. Consequently (34) means that X, Y and W diffuse incongruenty at the same time. Hence follows:

all diffusion-types are possible, except the incongruent.

From scheme I or (30) appears, therefore:

in system p all D.T. are possible, except N<sup>0</sup>. 5;

in system q all, except N<sup>0</sup>. 6;

in system r all, except N<sup>0</sup>. 2; etc.

For this reason N<sup>0</sup>. 5 in scheme Ip and N<sup>0</sup>. 6 in scheme Iq have been placed between parentheses.

Now we may say:

the composition of the liquids determines which of the diffusion-types is incongruent and, therefore, not possible;

the nature of the membrane determines which of the 7 other D.T. will occur.

We have been able to demonstrate this influence of the membrane experimentally in some cases, e.g. in an osmotic system in which the liquids consisted  $^{1}$ ) of :

$$X = Na_2S_2O_6$$
;  $Y = BaS_2O_6$ ;  $W = H_2O$ 

and of course had a special composition. Through a membrane, made of collodion three substances diffused, according to:

$$\longleftarrow X \longrightarrow Y \longleftarrow W \dots \dots \dots \dots (35)$$

Through a membrane, made of collodion, in which a little  $Cu_2 Fe(CN)_6$  had been deposed, they diffused, however, according to:

 $\longleftrightarrow X \longrightarrow Y \longrightarrow W \dots \dots (36)$ 

Consequently the water diffuses through the two membranes in opposite directions; so one of these directions is incongruent.

We also found this in this system, when one of the liquids had an other composition.

<sup>1)</sup> Comp. for this system: Exp. II and III.

Also in a system<sup>1</sup>), in which the liquids consist of  $X = NH_4Cl$ , Y = ammonium-succinate,  $W = H_2O$ , the D.T. depended on the membrane. The substance namely diffused according to (35) through a membrane: a. made of collodion; b. of a pig's bladder; c. of cellophan. According to (36) they diffused, however, through a membrane; d. made of collodion, in which a little  $Cu_2Fe(CN)_6$  had been deposed; e. of a pig's bladder, which had been treated in a special way; f. of parchment.

So here again it appears that water diffuses through some membranes towards the left and through other membranes towards the right.

We are able to extend the foregoing considerations to membranes, which transmit n substances; among other things we then find:

there exist  $2^n$  diffusion-types;

the composition of the two liquids determines which D. T. is incongruent and consequently can not occur;

the nature of the membrane determines which of the  $2^n-1$  other D. T. occurs.

Consequently if we take two liquids, containing e.g. five diffusing substances, then the diffusion may take place according to 32 types. If the two liquids are given a special composition, the membrane will determine which of the 31 possible D. T. will occur.

If, therefore, only the directions are known in which each of these substances passes through a membrane M(1) [viz. the substance X through a membrane M(X), the substance Y through a membrane M(Y), etc.], we know only very little. For this enables us to find the incongruent D. T, only, viz. that, according to which the substances cannot diffuse. The nature of the membrane now determines which of the 31 other D. T. will occur.

If besides we bear in mind that during the osmosis a membrane may change its nature and consequently its D.T. under all kinds of influences [e.g. the influence of the diffusing substances, age, hysteresis etc.]; we need not be surprised sometimes to see diffusions occur in vegetable or animal tissues, which perhaps were not expected, or when the direction of the diffusion of some substances should at times change in them.

Leiden, Lab. of Inorg. Chemistry.

(To be continued.)

<sup>1)</sup> This system will be published later on.