Chemistry. — *Osmosis of ternary liquids. Experimental part* III. By F. A. H. SCHREINEMAKERS and B. C. VAN BALEN WALTER.

(Communicated at the meeting of May 26, 1928).

In the preceding communications (Exp. I and II) we have discussed the apparent osmosis of some systems; now we shall consider their real osmosis, viz. the directions in which the substances pass through the membrane, etc.

First we shall briefly indicate in what way we have determined the point of intersection s_0 of two conjugated chords. For this purpose we imagine the points a and b on the one branch of a path and the points a' and b' on the other branch. We represent the composition of the liquid a by:

$$x_a \text{ quant. of } X + y_a \text{ quant. of } Y + (1 - x_a - y_a) \text{ quant. of } W$$

and that of the liquid a' by:

$$x'_a \text{ quant. of } X + y'_a \text{ quant. of } Y + (1 - x'_a - y'_a) \text{ quant. of } W$$

In order to represent the composition of the liquids b and b' we imagine the index a to be replaced by b.

The equation of the straight line, running through a and b is:

$$\frac{y - y_a}{y_a - y_b} = \frac{x - x_a}{x_a - x_b} \quad \ldots \ldots \ldots \quad (1)$$

We now put:

$$\mu = -\frac{y_a - y_b}{x_a - x_b} \qquad h = \mu\, x_a + y_a \quad \ldots \ldots \quad (2)$$

We now may substitute (1) by:

$$y = -\mu\, x + h \quad \ldots \ldots \ldots \quad (3)$$

The equation of the line $a'\,b'$ is:

$$\frac{y - y'_a}{y'_a - y'_b} = \frac{x - x'_a}{x'_a - x'_b} \quad \ldots \ldots \ldots \quad (4)$$

We now put:

$$\mu' = -\frac{y'_a - y'_b}{x'_a - x'_b} \qquad h' = \mu'\, x'_a + y'_a \quad \ldots \ldots \quad (5)$$

We now may substitute (4) by:

$$y = -\mu'\, x + h'. \quad \ldots \ldots \ldots \quad (6)$$

The equations (3) and (6) now define the x and y of the point of intersection s of the two chords; we find:

$$x = \frac{h - h'}{\mu - \mu'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

after which we find y from (3) or (6).

If we represent the angle formed by the chord $a\,b$ and the negative direction of the X-axis by φ then $\mu = tg\,\varphi$; besides we see that h is the part cut off the Y-axis by the chord $a\,b$. For μ' and h' the same is valid with respect to the chord $a'\,b'$.

We also see that we may substitute the index a by b in the values of h and h' of (2) and (5).

Now we began by determining μ and μ' and afterwards h and h' with the help of (2) and (5), afterwards x with the help of (7) and y with (3) or (6); then we knew the composition:

$$x \text{ quant. of } X + y \text{ quant. of } Y + (1 - x - y) \text{ quant. of } W$$

of the diffused mixture and consequently the position of the point s_0.

We shall just illustrate this deduction with an example; for this purpose we take the points 5 and 6 of the path of system V; we find it drawn schematically in fig. 1 Exp. I. It follows from table V:

$$x_5 = 7.312 \qquad y_5 = 7.620 \qquad x'_5 = 19.347 \qquad y'_5 = 1.070$$
$$x_6 = 9.188 \qquad y_6 = 7.255 \qquad x'_6 = 17.627 \qquad y'_6 = 1.408$$

in which all concentrations are expressed in procents. From (2) and (5) follows:

$$\mu = 0.19456 \qquad \mu' = 0.19651$$

and afterwards for h and h':

$$h = 9.043 \qquad h' = 4.872.$$

With the aid of (7) we now find:

$$x = -2139.$$

From (3) or (6) now follows: $y = 425$. As the concentrations have been expressed in procents, the W-amount is not $1 - x - y$, now, but $100 - x - y$ or $100 + 2139 - 425 = 1814$. Consequently the composition of the diffused mixture is:

$$-2139\,\%\,X + 425\,\%\,Y + 1814\,\%\,W \quad . \quad . \quad . \quad . \quad (8)$$

The diffused mixture is situated, therefore, in field IV (fig. 1, Gen. III).

From the position of this point s_0 with respect to the points 5 and 6, it appears that liquid 5 gives off this mixture; so we know that on part 5.6 of the path the mixture diffuses towards the right.

As the mixture contains negative quantity of X and a positive quantity of Y and W, this results for the directions, in which the substances pass through the membrane.

$$\overleftarrow{\;X\;} \qquad \overrightarrow{\;Y\;} \qquad \overrightarrow{\;W\;} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now we can also find the composition of the diffused liquid. For it appears from (8) that the substances X, Y and W have diffused through the membrane in the ratio:

$$2139 : 425 : 1814$$

If we now consider only the quantities and not the directions we see that:

$$2139 + 425 + 1814 = 4378$$

quantities have passed through the membrane; consequently the composition of the diffused liquid is:

$$48.9\ \% \ X + 9.7\ \% \ Y + 41.4\ \% \ W \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Consequently we find: the liquid which has passed through the membrane in the time during which the system passes along part 5 . 6 of the path, consists of 48,9 % of X which diffuse towards the left, and of 9,7 % of Y and 41,4 % of W which diffuse towards the right. So a greater volume goes through the membrane towards the right than towards the left.

It appears from the values of μ and μ' in (2) and (5) that numerator and denominator are usually small; a small mistake in the determination of the concentrations may sometimes cause a large mistake in μ and μ' and consequently in the position of the point s_0.

For this reason the compositions of the left and the right liquids have been determined as accurately as possible. It appeared from many duplo-determinations that the penultimate of the decimals given is absolutely correct. Yet in some cases the influence may be great, viz. when two points are situated close to one another and especially when the two chords approach each other closely towards the end of the osmosis.

The results of the calculations may be found in the tables and schemes of the preceding communications Exp. I and II.

In the schemes we find the directions in which the substances have passed through the membrane on the different parts of the path.

In the tables we find for each part of the path:

a. the field in which point s_0 is situated, and the direction in which this mixture has passed through the membrane.

b. sub X, Y and W the composition of the diffused liquid.

We find them for part 1 . 2 of a path with determination n^0. 2; for part 2 . 3 with determination n^0. 3; etc.

The compositions of the diffused mixtures have not been indicated in the tables, as they have no meaning by themselves; of course the liquids situated in field I have the same composition as the diffused liquid.

In a preceding communication (Gen. V) we have seen that we have to know the points s_l and s_r viz. the compositions of the mixtures L_l and

L_r in order to learn to know the real osmosis accurately. In order to find them, we must, however, know not only the compositions of the liquids on the right and the left side of the membrane, but also their quantities. Our experiments, however, have until now not enabled us to define this quantity with sufficient accuracy; in our considerations we have to limit ourselves to point s_0.

This point s_0, however, as we have previously (l.c.) seen, only represents an approximate value of the mixtures L_l and L_r diffusing in reality; for this reason the composition of the diffused liquid has been indicated in the tables in one decimal only.

Yet the s_0-scheme deduced from point s_0 generally indicates the directions in which the substances and the mixture pass through the membrane; we are shortly going to refer to the transition-cases, which have already been (l. c.) discussed before.

Towards the end of the osmosis the s_0-scheme, even when still in existence at the time is no longer dependable (l. c.); to this we may add as we have seen above, that the mistake in determining point s_0 may be big then. In some schemes also the horizontal arrows with the last parts of the path have been omitted for this very reason.

Notwithstanding all those difficulties of which we ourselves are only too well aware, we yet think ourselves justified in briefly discussing the real osmosis of these systems. This discussion, however, should be looked upon only as initial orientation for further investigations in this field.

If in the schemes we pay attention to the signs $>$ and $<$, which indicate whether the concentration of a substance on the left side of the membrane is larger or smaller than on the right side, and to the horizontal arrows which indicate the directions in which the substances pass through the membrane, we see that as well positive as negative osmosis occurs; in order to facilitate the survey, an asterisk has been placed with the horizontal arrows, which indicate a negative osmosis. We see from these schemes among other things the following:

the substance X diffuses in all systems in positive direction; II—V and in VII, however, also in negative direction;

the substance Y diffuses in all systems in positive direction; in III and IX, however, also in negative direction;

the substance W diffuses in all systems as well in positive as in negative direction.

As, however, the s_0-scheme is no more to be depended upon towards the end of the osmosis, we shall cancel all determinations in which the point s_0 is situated within field I; these parts of the path have been indicated in the schemes by the sign 0. Then we find:

the substance W diffuses in all systems in positive direction, but in I—III and VI—XII also in negative direction. We then find examples, as well of normal-normal-negative as of anormal-anormal-negative W-osmosis.

Consequently we may conclude from this that in reality besides positive-also negative osmosis occurs; this is what might be expected from a theoretical point of view also.

We shall consider some of the systems a little more in detail. First we take system XII the path of which has been represented schematically in fig. 1 Exp. II. It appears from the table that the mixture s_0 is situated in field IV during the total osmosis and goes towards the right. Consequently during all the osmosis the substance X goes towards the left (comp. scheme XII) and the substances Y and W towards the right.

Although, therefore, the water diffuses towards the left side during the whole of the osmosis, we yet have a positive osmosis on the part 1 . 6 of the path and on part 6 . 9 a negative W-osmosis; the reason for this is that the W-amount on part 1 . 6 is larger on the left side than on the right side, but on part 6 . 9 it is smaller on the left side than on the right side.

It appears from table V that the mixture s_0 of the part 1 . 6 of the path of system V (comp. fig. 1 Exp. I) is situated in field IV and diffuses towards the right; for part 6.8 of path s_0 is situated in field VII and diffuses towards the left. Consequently for the whole of part 1 . 8 obtains, as has been indicated also in the scheme, that X diffuses towards the left and Y and W towards the right (comp. Gen. V for the directions in which the mixtures L_l and L_r can diffuse at the moment that s_0 passes from field IV towards the opposite field VII).

The mixture s_0 of part 7 . 8 of the path is situated in field VII, that of part 8 . 9, however, in field VI; so in the vicinity of point 8 (viz. somewhere between 7 and 9) the mixture comes somewhere on the prolongation of the side $X\,Y$. As the mixture now does not contain W, no W passes through the membrane at this moment. We may represent the directions in which the water moves, by:

$$\xrightarrow{W} \quad \overset{W}{\text{---}} \quad \xleftarrow{W} \qquad \qquad (11)$$

The first arrow obtains when s_0 is still in field VII; the last, when s_0 has arrived in VI; the dash obtains for the moment that s_0 comes on the side $X\,Y$ and, therefore, no W diffuses.

Previously (Gen. V), however, we have already seen that in- and in the vicinity of such a point of transition small quantities of W yet will go towards the left or the right side, or are taken in or given off by the membrane. The s_0 scheme does not indicate these transitions; as we have seen above, (l.c.) we have to replace it in this case by a scheme, consisting of several groups.

But even, when the s_0-scheme should indicate the correct directions for the W-amount, the transition is not so simple as it has been represented above. For on the part 1.8 of the path the W-amount on the left side is larger than on the right side; on part 8.9, however, it is smaller on the left side than on the right side (comp. scheme V); in the vicinity of point 8, therefore, is situated a point, where both liquids have the same W-amount. Then, if we do not consider the direction in which the water diffuses, we have the symbol:

$$*\downarrow = \uparrow* \qquad \ldots\ldots\ldots \qquad (12)$$

Above, however, we saw that in the vicinity of point 8 also a transition, such as has been indicated in (11), is situated. If in (12) we now also indicate the direction, in which the water passes through the membrane, we see that one of the three symbols:

$$\underset{\xrightarrow{\qquad}\;*}{*\downarrow = \uparrow*} \qquad \underline{*\downarrow = \uparrow*} \qquad \underset{\xleftarrow{\qquad}\;*}{*\downarrow = \uparrow*} \qquad \ldots \qquad (13)$$

is possible with the transition; the center case will obtain only then when both points should happen to coincide.

It is apparent from table V that point s_0 passes from field VI towards I. We might be inclined to think that this takes place in a way corresponding to the transition from field VII towards VI; then at a certain moment of the osmosis point s_0 would arrive on the side WX, so that at this moment no Y would pass through the membrane; this, however, is not possible, as we shall see directly.

If we represent the angles formed by the chords with the negative direction of the X-axis by φ and φ', then, as we saw above, we have $tg\ \varphi = \mu$ and $tg\ \varphi' = \mu'$. Consequently the directions of the chords follow from the values of μ and μ'. In table Vb we find these values for all chords of this system.

If we leave chord 1.2 (and 1'.2') of the path out of consideration, we see that the angles φ and φ' increase perpetually during the osmosis; this is also valid, therefore, for the angles φ and φ' which are formed by the tangents with the negative direction of the X-axis. We now see from table Vb that somewhere in the vicinity of point 6 a point u (and u') is situated, where $\varphi = \varphi'$ and consequently the tangents run parallel. The point of intersection s_0 of these tangents is situated now at infinite distance in field IV or VII; now we have the transition of s_0 from field IV towards VII which has been discussed above.

In the vicinity of point q, however, is also situated a point v (and v') where the tangents become parallel again; now point s_0 is situated again at infinite distance, but it now passes from field VI toward field III.

The analysis indicates, however, that point s_0 of part 9.10 of the path is situated in field I; consequently point s_0 has passed from field III towards I either through field II or through IV.

When the system passes along part 9.10 of its path it is situated successively either in the fields VI, III, II and I or in VI, III, IV and I. The mixture s_0, experimentally determined, consists, therefore, of mixtures of very different fields.

This might perhaps be ascertained by having the system pass once more along part 9 . 10 of its path under precisely the same circumstances and by determining several points on this same part; but even, if this were possible, these points would be situated too close to one another for us to deduct from them the mixture s_0 with sufficient accuracy.

Previously (Gen. V) we have seen already that the form of a path also depends on the quantity and composition of the liquid, contained by the membrane at every moment of the osmosis.

TABLE V*b*.

	$\mu = tg\,\varphi$	$\mu' = tg\,\varphi'$
1.2	0.13469	0.15576
2.3	0.09678	0.13264
3.4	0.10009	0.14182
4.5	0.13163	0.16578
5.6	0.19456	0.19651
	u	u'
6.7	0.29739	0.29252
7.8	0.44744	0.43070
8.9	0.97485	0.72578
	v	v'
9.10	1.0167	1.3558

If we take a membrane, as e.g. a pig's bladder or a piece of parchment that contains none of the diffusing substances, then this must first take in these substances before the osmosis can begin.

If we take a membrane, which already contains water, as e.g. collodion, then it still has to absorb the other substances, whereas it will perhaps give off water.

The form of the path, especially at the beginning of the osmosis, therefore, also depends more or less on the original condition of the membrane. Of course this change in form is no mistake of the system; it only indicates which changes have occurred on the left and on the right side of the membrane; it is the cause, however, that the mixture L_0 in this first part of the path shows a greater deviation from the mixtures L_l and L_r.

It is apparant from table V^b that the angle φ is larger on part 1 . 2 of the path than for part 2 . 3 but afterwards increases all the time; the same is valid for the angle φ'. Therefore, at the beginning of the osmosis both branches of the path have another form than at a later time. A similar phenomenon also occurs with several of the other paths.

Perhaps this is a result of the influence of the membrane at the beginning of the osmosis, as has been discussed above.

The path of system IV practically coincides with part V in fig. 1 Exp. I; it appears from the schemes that for system IV the same is valid as for V. Yet system IV shows a peculiarity which does not occur in V.

It namely appears from the table that point s_0, after having passed from field V towards VII, returns again to IV and then again passes towards VII; duploexperiments showed that mistakes in analysis did not play a part here. These leaps and bounds of the point s_0, however, have no influence on the directions in which the substances pass through the membrane, as is apparent from the scheme; of course they do influence the ratio of the quantities of these substances; in field IV less X goes towards the left than $Y + W$ towards the right; in field VII the opposite thing is the case.

Perhaps this phenomenon can spring from different cases; we have to bear in mind here, that with these leaps and bounds the tangents run practically parallel. For the path now is not theoretical, but experimental; it consists of a succession of theoretical parts, which indeed pass into one another continuously, but yet do not belong to the same theoretical path. (Comp. Gen I); besides the temperature during the whole of the osmosis has not remained constant.

The changes, which the diffusing substances cause in the membrane during the osmosis, can be of more influence, however; this alteration can continuously change the permeability for one or more of the substances. We have had membranes [collodion + deposit $Cu_2\ Fe\ (C\,N)_6$] which had practically lost their permeability altogether after an osmosis of some days; after having been put into water some of them partially got it back again, others, however, did not.

For the systems II and III, the paths of which in fig. 1 Exp. I are situated between the paths I and V, the same is valid as for system V. In discussing this latter system we have seen that during its transition from field VI towards I point s_0 is situated successively in the fields VI, III, II and I or in VI, III, IV and I. As point s_0 of system II has been determined, however, also in field IV, it has here run through the fields VI, III, IV and I successively.

A study of the movement of point s_0 in the other systems is left to the reader.

Previously (Gen. II) we have seen already that no direct correspondance exists between the direction in which one of the substances passes through the membrane and the change in concentration of this substance on both sides of the membrane. Of this we find many examples in these systems. Let us take system VI e.g. We see that substance Y diffuses towards the right on the parts 1.2 and 2.3 of the path; yet the Y-amount of both liquids increases. On part 7.8 of the path the water diffuses towards the right; yet the W-amount still decreases on the right side and increases on the left side.

The left-side liquids L_1 of the systems I—V only contain water + Na_2CO_3; approximately they have the same composition. The right-side liquids L'_1 contain water + $Na\,Cl$; they have very different compositions, however. Therefore, the five paths in fig. 1 Exp. I have on the Y-axis the same point 1 but on the X-axis a different point 1′. For the W-amount of part 1.2 of these paths is valid:

$$\text{I} \longleftarrow \qquad \text{II—V} \longrightarrow$$

The first arrow obtains for system I, the second for the systems II—V. From this we learn the influence of the concentration of the right-side liquid on the direction, in which the water passes through the membrane.

The systems VI and VII (fig. 1. Exp. II) approximately have the same liquids on the left and the right side of the membrane. They have a different membrane, however. For the W-amount of part 1.2 of these paths we have:

$$\text{VI} \longrightarrow \qquad \text{VII} \longleftarrow$$

For the systems XI and XII which also have approximately the same liquids on the left and the right side of the membrane (fig. 2 Exp. II) the same obtains.

Previously we have seen already that the membrane has a great influence on the duration of the osmosis; we see here that it can influence the very direction in which the water passes through the membrane.

Leiden, Lab. of Inorg. Chemistry.