Chemistry. — *Osmosis of ternary liquids. General considerations* V.
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(Communicated at the meeting of April 28, 1928).

The diffusing mixture and the real membrane.

In the preceding communications (Gen. III and IV) we have seen in what way the composition of the diffused mixture can be found and how from this the directions in which the different substances pass through the membrane may be deduced, the composition of the diffused liquid, etc. We have seen that the composition of the diffused mixture, which we shall call L_0, is represented by the point of intersection S_0 of two conjugated chords. This is only the case, however, when the membrane itself does not contain the diffusing substances; as, however, the membrane does contain these substances, we shall call the first a "theoretical" and the second a "real" membrane.

In fig. 1 two points of the one branch of an osmosis-path are represented by 1 and 2 and two points of the other branch by 1′ and 2′. In point 1 (and 1′) of the path we imagine an osmotic system with a real membrane; we represent this by:

$$l_1 \times L_1 \mid m_1 \times M_1 \mid r_1 \times L'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

On the left side of the membrane there are l_1 quantities of a liquid L_1 and on the right side r_1 quantities of a liquid L'_1. We represent the composition of L_1 by:

$$x_1 \text{ quant. of } X + y_1 \text{ quant. of } Y + (1 - x_1 - y_1) \text{ quant. of } W \quad . \quad (2)$$

and that of L'_1 by:

$$x'_1 \text{ quant. of } X + y'_1 \text{ quant. of } Y + (1 - x'_1 - y'_1) \text{ quant. of } W \quad . \quad (3)$$

Although the substances will not be equally spread in the membrane, yet we may say that it contains a definite quantity of liquid of a definite composition. We shall say that the membrane contains m_1 quantities of a liquid M_1, the composition of which we shall represent by:

$$\alpha_1 \text{ quant. of } X + \beta_1 \text{ quant. of } Y + (1 - \alpha_1 - \beta_1) \text{ quant. of } W \quad . \quad (4)$$

We imagine this liquid M_1 to be represented in fig. 1 by the point 1″. In the point 2 (and 2′) of the path we then have an osmotic system:

$$l_2 \times L_2 \mid m_2 \times M_2 \mid r_2 \times L'_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In order to represent the compositions of these liquids we imagine in (2), (3) and (4) the index 1 to be substituted by 2. The liquid M_2 of the membrane has been represented in fig. 1 by point 2″.

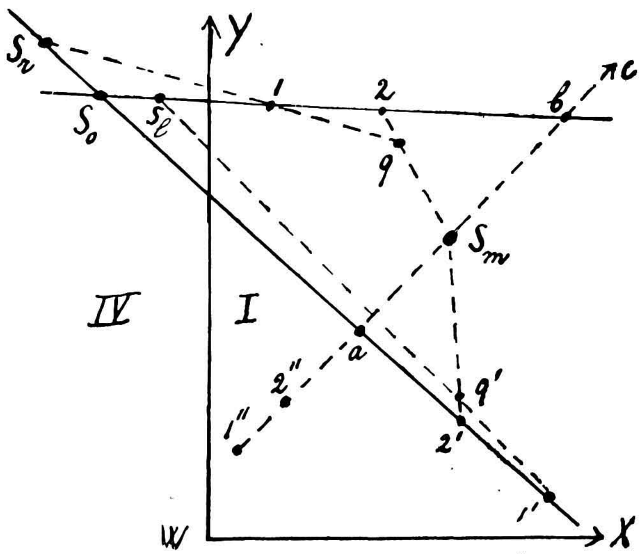

Fig. 1.

Consequently the osmosis-path of the system does not consist of 2, but of three branches; if namely the left side liquid travels along the part 1 . 2, and, therefore, the right side liquid along the part 1′ . 2′, then the membrane travels along the part 1″ . 2″ of the path.

If the left side liquid gives off a certain quantity u of a substance, then the right side liquid will take in a quantity, smaller or larger than u, according as the membrane will take in or give off a little of this substance during that time; it may even be supposed that as well the left side liquid as the right side liquid give e.g. the substance X to the membrane or take it from the membrane. For this reason we cannot speak any more of a single diffused mixture, but we shall distinguish three mixtures; we call them L_l, L_m and L_r and represent them in fig. 1 by the points s_l, s_m and s_r.

L_l is the mixture which is taken in or given off by the left side liquid. As L_1 has passed into L_2 by taking in or giving off a certain quantity of L_l, s_l, therefore, must be situated somewhere on the line 1 . 2. If s_l is situated in the way drawn in fig. 1, then this mixture has been given off by the left side liquid. We represent the composition of this mixture by:

$$x \text{ quant. of } X + y \text{ quant. of } Y + (1 - x - y) \text{ quant. of } W. \quad (6)$$

L_m is the mixture, which is taken in or given off by the membrane; consequently the point s_m is situated somewhere on the line 1″ . 2″. In fig. 1 it has been assumed that this mixture has been taken in by the membrane. We represent its composition by:

α quant. of $X+\beta$ quant. of $Y+(1-\alpha-\beta)$ quant. of W . . (7)

L_r is the mixture which is taken in or given off by the right side liquid; consequently the point s_r is situated somewhere on the line $1'.2'$. In fig. 1 we have assumed that this mixture has been taken in by the right side liquid. We represent its composition by:

x' quant. of $X+y'$ quant. of $Y+(1-x'-y')$ quant. of W . (8)

Now we shall assume that the left side liquid has given off l quantities of L_l and the membrane has taken in m quantities of L_m and the right side liquid r quantities of L_r.

It appears from the liquids L_1 and L_2 on the left side of the membrane that during the osmosis l_1-l_2 quantities have disappeared here; they contain $l_1 x_1 - l_2 x_2$ quantities of X and $l_1 y_1 - l_2 y_2$ quantities of Y; of course the remainder is the substance W. Consequently we find:

$$l=l_1-l_2 \quad x=\frac{l_1 x_1 - l_2 x_2}{l} \quad y=\frac{l_1 y_1 - l_2 y_2}{l} \quad . \ . \ . \ (9)$$

From the liquids in the membrane and on the right side of it, follows:

$$m=m_2-m_1 \quad \alpha=\frac{m_2 \alpha_2 - m_1 \alpha_1}{m} \quad \beta=\frac{m_2 \beta_2 - m_1 \beta_1}{m} \quad . \ . \ (10)$$

$$r=r_2-r_1 \quad x'=\frac{r_2 x'_2 - r_1 x'_1}{r} \quad y'=\frac{r_2 y'_2 - r_1 y'_1}{r} \quad . \ . \ (11)$$

As the quantities of the substances do not change during the osmosis, we have:

$$\left.\begin{aligned} l_1+m_1+r_1&=l_2+m_2+r_2 \\ l_1 x_1+m_1 \alpha_1+r_1 x'_1&=l_2 x_2+m_2 \alpha_2+r_2 x'_2 \\ l_1 y_1+m_1 \beta_1+r_1 y'_1&=l_2 y_2+m_2 \beta_2+r_2 y'_2 \end{aligned}\right\} \quad . \ . \ . \ . \ (12)$$

With the aid of (9), (10) and (11) we find from this:

$$l=m+r \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (13)$$

$$l x=m \alpha+r x' \qquad l y=m \beta+r y'$$

If we consider the compositions of the mixtures L_l, L_m and L_r then it follows from (13):

$$l \times L_l = m \times L_m + r \times L_r \quad . \ . \ . \ . \ . \ . \ (14)$$

This expresses that the entire mixture, which has disappeared from the left side liquid, has been taken in by the membrane and the right side liquid. As this speaks for itself, we are able to write down (14) without any further deduction. It now follows from (14):

the point s_l is situated between s_m and s_r and divides the line into two parts, which are determined by:

$$s_l s_r : s_l s_m = m : r \quad . \ . \ . \ . \ . \ . \ . \ . \ (15)$$

We shall now assume that, besides the compositions of the left side and right side liquids, their quantities l_1, l_2, r_1 and r_2 are known also. Then we are able to determine l, x and y from (9) and r, x' and y' from (11). Next we find m, α and β from (13). Consequently we know the quantities and the compositions of the three diffused mixtures.

Matters are otherwise, however, if we only know the compositions of the left side and right side liquids. Then the point S_0 is indeed known but not the points S_l and S_r, which are essential in order to determine the directions in which the substances now pass through the membrane. Yet in many cases it is possible to find these directions with the aid of point S_0 only, as will be shown later on.

When system (1) has passed into (5), then the membrane has taken in m quantities of L_m. We now put these m quantities in the left side liquid L_2; this now changes its composition and passes again into a liquid L_q which has been represented in fig. 1 by point q. This liquid has been formed from l_2 quantities of L_2 and m quantities of L_m; consequently point q is situated on the line $2 \,.\, S_m$ and it divides this line into two parts, which are determined by:

$$q \,.\, 2 : q \,.\, s_m = m : l_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

So, instead of system (5) we now get the system:

$$(l_2 + m) \times L_q \;\vert\; m_1 \times M_1 \;\vert\; r_2 \times L'_2 \quad . \quad . \quad . \quad . \quad . \quad (17)$$

so that the membrane has not changed its composition in passing from (1) to (17); consequently the diffused mixture is represented by the point of intersection of the lines $1 \,.\, q$ and $1' \,.\, 2'$. As the state of things on the right side of the membrane in (17) is now the same as in (5), the mixture L_r must have diffused; consequently point s_r is the point of intersection of the lines $1 \,.\, q$ and $1' \,.\, 2'$.

If we put the m quantities of L_m in the right side liquid, then we get the system:

$$l_2 \times L_2 \;\vert\; m_1 \times M_1 \;\vert\; (r_2 + m) \times L'_q \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The liquid L'_2 of (5) has now been replaced by a liquid L'_q which is situated in fig. 1 on the line $2' \,.\, s_m$; for this obtains:

$$q' \,.\, 2' : q' \, s_m = m : r_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

As the state of things on the left side of the membrane now is the same in (18) as in (5), the point of intersection of the lines $1 \,.\, 2$ and $1' \,.\, q'$ falls in the point s_l. Consequently we find:

s_l is the point of intersection of the chord $1 \,.\, 2$ with the line $1' \,.\, q'$
s_r is the point of intersection of the line $1 \,.\, q$ with the chord $1' \,.\, 2'$.

In fig. 1 s_r is situated on the left side and s_l on the right side of s_0; this is the case when s_m is situated between a and b; if, however, s_m

is situated between $2''$ and a, so that point q' comes on the other side of the chord $1'.2'$, then we see that both points come on the left side of s_0. If, however, s_m is situated between b and c (we imagine c at infinite distance) then both points fall on the right side of s_0.

In the transition-cases, viz. when s_m is situated in a or in b, then s_l or s_r coincide with s_0.

We are able to express the length of the lines $s_0 s_l$ and $s_0 s_r$ in different ways. A simple way of expressing it is among others:

$$s_0 s_l = \frac{m}{l} \cdot \beta \qquad s_0 s_r = -\frac{m}{r} \cdot \alpha \quad . \quad . \quad . \quad . \quad . \quad (20)$$

in which, however, α and β have another meaning than above, though they are connected with them. We are able to deduce these equations in different ways, one of which we shall briefly indicate.

It is namely possible to prove that the equations (13) obtain for each system of coordinates; we now choose the point s_0 as origin, the line $s_0 1'$ as X-axis and the line $s_0 1$ as Y-axis. Then α is the distance of s_m to the line $s_0 1$, measured along a line parallel to the line $s_0 1'$; β is the distance of s_m to the line $s_0 1'$, measured along a line parallel to $s_0 1$.

For the point s_l now obtains $x = 0$ and $y = s_0 s_l$ and for point s_r we find $x' = s_0 s_r$ and $y' = 0$. Substituting these values in (13) we find (20).

In fig. 1 α and β are both positive; now (20) gives a positive value for $s_0 s_l$ and a negative value for $s_0 s_r$; we see that this is in accordance with fig. 1.

From what precedes it appears that the points s_l and s_r can be situated in different ways with respect to s_0; it follows from (20) that the smaller m is with respect to l and r, the nearer they will be to s_0. For the present we shall leave it so; to the other case we are going to refer later on.

Above we have noticed already that we have to know the points s_l and s_r in order to determine the composition of the diffusing mixtures and the directions in which they and the substances pass through the membrane. In order to consider what mistakes may arise, if we use the point s_0 instead of these points, we shall discuss a few cases.

First we shall suppose the point s_0 to be in field IV not too close to one of the sides (or their prolongations) of the triangle, so that the points s_l and s_r will be situated in this field as well.

If we were to use the point s_0 now, then we should make a mistake in the determination of the mixtures L_l and L_r which really have diffused and of course this will always be the case, when the points do not coincide.

The directions, in which the three substances and their mixtures pass through the membrane, are, however, also indicated by the point s_0.

The same obtains also for other fields, except, as we shall see later on, towards the end of the osmosis.

Now we assume that during the osmosis point s_0 passes from field IV to field I; as in this case no divergences of the substances Y and W occur, we need only consider the substance X.

As long as s_0 is situated in field IV, the mixture contains a negative quantity of X; as liquid 1 gives off this mixture, a negative quantity of X will go towards the right; so the substance X will really go towards the left.

If s_0 comes on the side WY, so that the mixture does not contain X, then no X will consequently pass through the membrane.

If s_0 comes in field I then the mixture contains a positive quantity of X; now the substance X passes through the membrane towards the right. Point s_0 now yields the simple scheme:

$$\underset{\longleftarrow}{X} \qquad \underset{\text{———}}{X} \qquad \underset{\longrightarrow}{X} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (21)$$

The first symbol obtains when s_0 is situated in field IV, the second when s_0 is situated in field I; the dash indicates that at that moment no X passes through the membrane.

Each of the points s_l and s_r indicates a similar scheme as (21); yet there is a difference viz. the transition-symbol occurs in these three schemes at different moments of the osmosis.

We now shall assume that the points are situated with respect to one another as shown in fig. 1; then point s_l will be the first to come on the side WY, next point s_0 and at last s_r. If the three systems are combined to form one, we get scheme (22).

	1	2	3	4	5	6	7	
S_l	$\longleftarrow$	———	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	S_l
S_r	$\longleftarrow$	$\longleftarrow$	$\longleftarrow$	$\longleftarrow$	$\longleftarrow$	———	$\longrightarrow$	S_r . . (22)
S_0	$\longleftarrow$	$\longleftarrow$	$\longleftarrow$	———	$\longrightarrow$	$\longrightarrow$	$\longrightarrow$	S_0

The top row (at the beginning and the end of which s_l has been placed) represents the s_l-scheme; we call these arrows and directions the s_l-arrows and s_l-directions. Consequently these arrows indicate what has really been happening to the left side liquid. Therefore, an arrow pointing to the left indicates that the left side liquid takes in X, an arrow pointing to the right that this left side liquid gives off X.

The middle row is the s_r-scheme. The s_r-arrows indicate, therefore, what really happens to the right side liquid. Consequently an arrow pointing to the left indicates that the right side liquid gives off X, an arrow pointing to the right that this right side liquid takes in X.

The lowest row is the s_0-scheme; consequently the s_0-arrows only indicate what can be deduced from point s_0; now we must consider in how far they are in accordance with reality.

For this purpose we divide (18) into seven groups.

Group 1 obtains as long as the three points are still situated in field IV.

Group 2 obtains when s_l comes on the side WY.

Group 3 obtains when s_l is in field I but the other points still in IV.

Group 4 obtains when s_0 comes on the side WY.

Group 5 obtains when s_r is still in IV, but the other points already in I.

Group 6 obtains when s_r comes on the side WY.

Group 7 obtains when the three points are situated in field I.

From this now appears:

in group 1 and 7, so when the three points are situated at the same time either in field IV or in field I, the s_0-arrow indicates the real direction, in which the substance X passes through the membrane; in the transition-groups 2—6 this is no more the case.

Let us e.g. take group 2. It appears from the s_l-dash that the left side liquid does not absorb or give off X at that moment; it follows from the s_r-arrow that the right side liquid gives off X; consequently this has been absorbed by the membrane.

The s_0-arrow, therefore, does not completely concur with reality; for it indicates that X from the right side liquid has gone towards the left side liquid; in reality, however, X has gone from the right side liquid towards the membrane.

It is also clear that the s_0-arrows cannot fully represent the state of things in the other transition-groups either; in each of these groups the s_l- and s_r-arrows namely have contrary direction; consequently they cannot be replaced by a single arrow.

Further consideration of what is really happening in the groups 3—6 is left to the reader.

So we find the following:

the s_0-scheme corresponds with reality as long as point s_0 does not approach one of the sides of the triangle too much; in the vicinity of side WY, however, it obtains no more for the substance X and we have to replace it by the s_l- and s_r-schemes. In general the quantities of X duffusing during these transitions, are small.

Of course the same things obtain for the substances Y or W when point s_0 arrives in the vicinity of the sides WX or XY.

Previously (Gen. III fig. 3) we have already seen that point s_0 can also pass from field IV towards VII during the osmosis; this is the case when the chords 1 . 2 and 1′. 2′ (fig. 1) become parallel.

As long as s_0 is situated in field IV we have the scheme:

$$\underset{\longleftarrow}{X} \quad \underset{\longrightarrow}{Y} \quad \underset{\longrightarrow}{W} \quad \ldots\ldots\ldots \quad (23)$$

Then namely the left side liquid gives off a mixture s_0, which contains a negative quantity of X but a positive quantity of Y and W.

When s_0 comes in field VII, then the left side liquid absorbs this mixture; this, however, now contains a positive quantity of X and a negative quantity of Y and W; consequently we again get scheme (23).

At the moment that s_0 passes from field IV towards VII, scheme (23) obtains as well as we have previously (Gen. III) seen. Remarkable is only that at this moment as much of X diffuses towards the left as Y and W towards the right.

Consequently we get the scheme (23) no matter whether s_0 is situated in field IV or VII; as this also obtains for the points s_r and s_l we find, therefore:

when point s_0 passes from field IV towards VII; then the s_0-scheme indicates the directions in which the substances really pass through the membrane.

It is easy to see, however, that this is no more the case for the directions, in which the mixtures L_l and L_r pass through the membrane. For this another scheme with five transition-groups may be deduced; in these cases, however, the quantities of the diffusing mixtures are generally small. The deduction of these schemes I leave to the reader.

In a system with a theoretical membrane the composition of the mixture which really passes through the membrane, is represented by s_0; this point, therefore, can never be situated as shown in figs. 2 or 3.

In fig. 2 namely s_0 is situated between the points 1 and 2 and it is clear that L_1 can never pass into L_2 by absorbing or giving off this mixture s_0. Consequently the point s_0 cannot be situated between 1′ and 2′ either. Of course s_0 cannot be situated as drawn in fig. 3, for then L_1 as well as L_2 should have to absorb this mixture.

Fig. 2.

Fig. 3.

In a system with a real membrane the mixtures, really absorbed or given off on the left and on the right side, are represented by s_l and s_r. It is clear now that s_l, which must be situated on the chord 1 . 2, can never be situated between the points 1 and 2; the point s_r which must be situated on the chord 1′ . 2′ can never be situated between the points 1′ and 2′. Although in a system with a theoretical membrane the point s_0 cannot be situated as drawn in figs. 2 and 3, this is actually the case in a system with a real membrane, especially when the points 2 and 2′ draw nearer to each other.

We imagine that system (1) approaches its final condition without changing the composition of its membrane; then the liquids become equal on both sides of the membrane. We represent this system by:

$$l_e \times L_e \mid m_1 \times M_1 \mid r_e \times L_e \quad \ldots \ldots \quad (24)$$

The final liquid l is now represented in fig. 4 by a point e on the

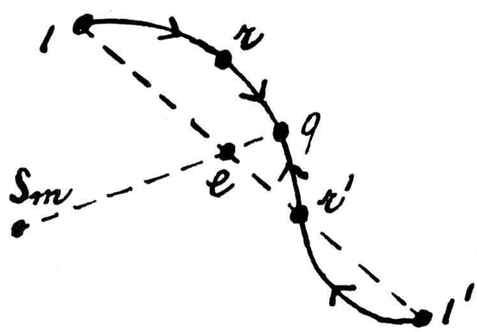

Fig. 4.

line 1 . 1'. As, however, the membrane has absorbed m quantities of a mixture L_m, the system (24) will not come into existence in reality, but a system:

$$l_q \times L_q \mid m_q \times M_q \mid r_q \times L_q \quad \ldots \ldots \quad (25)$$

This liquid L_q has another composition than L_e and has been represented in fig. 4 by point q. If we represent the composition of L_m by the point s_m, then q must be situated on the prolongation of the line $s_m e$. We now find:

$$eq = \frac{m}{r_1 + l_1 - m} \times e S_m \quad \ldots \ldots \quad (26)$$

Consequently the position of the point q depends on the quantity of m and the composition of the mixture L_m which has been absorbed by the membrane. From this appears among other things that even the position of point q depends on the dimensions of the membrane.

Instead of a path with the final point e on the line 1 . 1' we consequently get a path, which has been shifted a little and has its point in q.

Branch 1'. q of this path now intersects the line 1 . 1' in a point r'; consequently a point r conjugated with r' must be situated on branch 1 . q.

If the liquid 2 is situated between r and q consequently 2' between r' and q then we see that the point of intersection s_0 of the chords 1 . 2 and 1'. 2' is situated as drawn in fig. 2.

If branch 1'. q did not intersect the line 1 . 1' then s_0 would be situated as drawn in fig. 3.

Consequently we see that towards the end of the osmosis point s_0

can be situated as drawn in the figs. 2 and 3; it is clear that in this case no s_0-scheme can be formed any more.

So the following things appear among others from our considerations.

If we only know the compositions of the liquids on the left and the right side of the membrane, then we can only find the point s_0; this gives only approximated values for s_l en s_r.

In general the s_0-scheme indicates the exact directions, in which the different substances and the mixtures L_l and L_r go through the membrane; it is, however, no longer absolutely valid for any of the substances, when the point s_0 comes in the vicinity of one of the sides of the triangle (e.g. for the substance X in the vicinity of the side WY).

neither does it obtain absolutely any more for the direction of the diffusing mixture when s_0 is situated at infinite distance (e.g. with the transition from field IV towards field VII).

It is of no use towards the end of the osmosis.

If, however, not only the compositions, but also the quantities of the liquids on the left and the right side of the membrane are known, then we can find L_l and L_r and they enable us to determine accurately what has been happening during the osmosis.

(To be continued.)

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