Chemistry. — *Osmosis of ternary liquids. General considerations.* I.
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In previous communications [1]) which will be continued, I have discussed some equilibria, which may occur in systems, in which one or more semipermeable membranes are present. As, however, membranes, which let some of the dissolved substance pass, and others not, are difficult to make in a serviceable state [2]), now I have undertaken in collaboration with Mr. B. C. VAN BALEN WALTER an experimental investigation on the progress of the osmosis, if membranes are used, which are permeable for all substances. In order to facilitate the discussion of the results, which are sometimes very remarkable at first sight and in order to give some survey of that which is to be expected in this sphere, it is necessary to begin with some general considerations. As our experimental investigations, which will be published afterwards, relate to liquids, which consist of three substances, I shall limit myself in my considerations to these liquids.

1. *The theoretical osmosis-path.*

We take a liquid L consisting of three substances, which we shall call X, Y and W; although it is not of the least importance for the further considerations, we shall say that W represents water; we may imagine arbitrarily to be the substances X and Y e.g. $NaCl$ and Na_2CO_3 or sugar and ureum, etc.

We represent the composition of this liquid L by:

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

in which we mean by "quantities" either quantities of weight or mol-quantities. Of course in general it is indifferent in which of those "quantities" we express the composition; yet we shall see afterwards that in some cases we have to pay attention to it.

We are able to represent the composition of a liquid in the well

[1]) F. A. H. SCHREINEMAKERS. These Proceedings, **27**, 701 and the 23 following communications.

[2]) In his book "The osmotic pressure of Aqueous Solutions" K. N. MORSE describes a method of making membranes, which are permeable for water only. Although those membranes are quite fit for that purpose, we cannot use them, because they transmit the water too slowly.

known way graphically in a concentration-diagram; for this purpose we take a triangle, the anglepoints of which represent the substances X, Y and W; we choose this triangle equilateral or rectangular equilateral. In fig. 3 the sides WX and WY of a similar triangle are partly drawn.

Now we shall represent the osmotic system, which arises, if we bring in osmotic contact bij means of a membrane the liquids L_1 and L'_1 by:

$$L_1 \mid L'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we wish to express also that there are n_1 quantities of the liquid L_1 and n'_1 quantities of the liquid L'_1, then we represent it by:

$$n_1 \times L_1 \mid n'_1 \times L'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the membrane is transmitting the three substances, then this system cannot be in equilibrium, unless both liquids have the same composition.[1] Consequently the substances X, Y and W must diffuse through the membrane in some direction and this osmosis will continue as long as the liquids on both sides of the membrane get the same composition; we represent this final-liquid by L_e.

If we represent the composition of L_1 by:

x_1 quant. of $X + y_1$ quant. of $Y + (1 - x_1 - y_1)$ quant. of W (2ª)

and that of the liquid L'_1 by

x'_1 quant. of $X + y'_1$ quant. of $Y + (1 - x'_1 - y'_1)$ quant. of W (2ᵇ)

and that of the final-liquid by:

x_e quant. of $X + y_e$ quant. of $Y + (1 - x_e - y_e)$ quant. of W

then we find easily:

$$x_e = \frac{n_1 x_1 + n'_1 x'_1}{n_1 + n'_1} \qquad y_e = \frac{n_1 y_1 + n'_1 y'_1}{n_1 + n'_1} \quad . \quad . \quad . \quad (3)$$

Therefore the composition of the final-liquid L_e does not only depend on the compositions of the liquids L_1 and L'_1 but also on the quantities n_1 and n'_1 which are present in system (2).

We represent the liquids L_1 and L'_1 of system (2) in fig. 1 by the points 1 and 1′. In order to save room the anglepoints of the sides of the concentration-triangle WXY are omitted in this figure. We represent the final liquid L_e by a point e which is of course somewhere on the straight line $1 . 1'$. The composition of the final-liquid e and therefore also the position of the point e depends on the ratio $n_1 : n'_1$ consequently

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[1]) If the three substances form a system, in which dimixtion into two liquids can occur, then system (2) can also be in equilibrium when L_1 and L'_1 are different. Then, however, L_1 and L'_1 represent two liquids, which can exist next to one another if we take away the membrane.

on the ratio of the quantities of the liquids on the left and on the right side of the membrane. The point e divides the line $1.1'$ into two parts $e.1$ and $e.1'$ the lengths of which are defined by:

$$e.1 : e.1' = n'_1 : n_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to pass into the final-liquid L_e the liquid L_1 will go along a path, which starts from point 1 and finishes in point e; this path which we shall call the „osmosis-path of the liquid L_1" is represented in fig. 1 by curve $1.2.3....e$; the arrows indicate the direction in which the liquid travels along this path during the osmosis. The same is valid for the liquid L'_1; its osmosis-path is indicated by curve $1'.2'.3'...e$. Those two osmosis-paths of the liquids form together the osmosis-path of system (2).
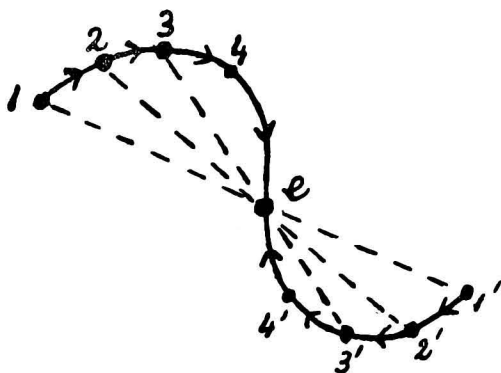
After some time the liquids L_1 and L'_1 of this system will have changed their composition; e.g. the left has arrived at point 2 and the right in point $2'$; we now call those liquids L_2 and L'_2. As the quantities of the liquids on both sides of the membrane change also during the osmosis, we represent them now by n_2 and n'_2. Consequently system (2) has passed into the system:

Fig. 1.

$$n_2 \times L_2 \mid n'_2 \times L'_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As the total quantity of both liquids does not change during the osmosis, must be $n_2 + n'_2 = n_1 + n'_1$. As also the total composition of the whole system remains constant, the line $2.2'$ must also go through the point e. Instead of (4) we now have:

$$e.2 : e.2' = n'_2 : n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Some time afterwards the liquids have arrived in the points 3 and $3'$; we then have the osmotic system:

$$n_3 \times L_3 \mid n'_3 \times L'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For this is valid:

$$n_3 + n'_3 = n_2 + n'_2 = n_1 + n'_1.$$

Of course the line $3.3'$ goes also through the point e; we now have:

$$e.3 : e.3' = n'_3 : n_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Of course the same thing holds good also when the liquids are in other points of their paths, e.g. in 4 and $4'$; of course the line $4.4'$ goes also through point e.

We shall call liquids which are present at a same moment on both

sides of the membrane, as e. g. L_1 and L'_1 or L_2 and L'_2 etc. „conjugated liquids". The lines which unite two conjugated points, as e.g. 1.1' or 2.2' etc. are called „conjugation-lines". From the above now follows:

the conjugation-lines of an osmosis-path all go through the point which represents the composition of the final-liquid; the ratio of the parts into which this point divides the conjugation-lines, is equal at any moment to the ratio of the quantities of the liquids which are present at that moment on both sides of the membrane.

On the reverse: every straight line, going through the point e, which intersects the osmosis-path is a conjugation-line; as the points of intersection represent two liquids which will be present at a definite moment on both sides of the membrane.

If we draw tangents to the osmosis-path in two conjugated points e.g. in 1 and 1' or 2 and 2' then we call them "conjugated tangents"; if in the one path we draw a chord e.g. 1.2 or 2.3 etc. and in the other path the corresponding chord e.g. 1'.2' or 2'.3' etc., then we call them "conjugated chords". Later we shall see how we can make use of the conjugated tangents and chords in order to deduce the directions and the ratios in wich the different substances diffuse through the membrane at definite moments.

If in the osmotic system (2) we take two definite liquids L_1 and L'_1 then the osmosis-path starts in fig. 1 from the points 1 en 1'; the form of the path, however, still depends on many factors; some of them are:

a. the quantities n_1 and n'_1 of the liquids on both sides of the membrane;

b. the membrane through which the osmosis takes place;

c. the temperature and pressure.

The influence of that mentioned sub a is evident; above we have indeed seen already that the position of point e depends on the ratio $n_1 : n'_1$ consequently on the ratio of the quantities of the liquids L_1 and L'_1.

If we take the same quantity of liquid on both sides of the membrane, so that $n_1 = n'_1$ then as becomes apparent from (4) also $e.1 = e.1'$; then the point e is situated, as in fig. 2, in the middle of the line 1.1'; then the osmosis-path can have a form as curve 1 e 1'.

If, however, we take more of the liquid L_1 so that $n_1 > n'_1$, then follows from (4) that $e.1' > e.1$; so the final-point e is situated nearer to point 1; it is represented in fig. 2 by point q. Consequently the osmosis-path must now have also another form; it is represented by 1 q 1'.

If we take more of the liquid L'_1 so that $n_1 < n'_1$ then follows that the final-point e must be situated nearer to point 1'; it is represented in fig. 2 by point r; the osmosis-path now can have a form as curve 1r1'.

We shall afterwards discuss some examples of such paths.

Of course for each of these paths is true that the conjugation-lines go through one point; these of path $1 \, q \, 1'$ all go through point q; these of path $1 \, e \, 1'$ through point e and these of path $1 \, r \, 1'$ through point r.
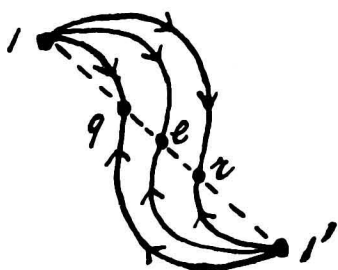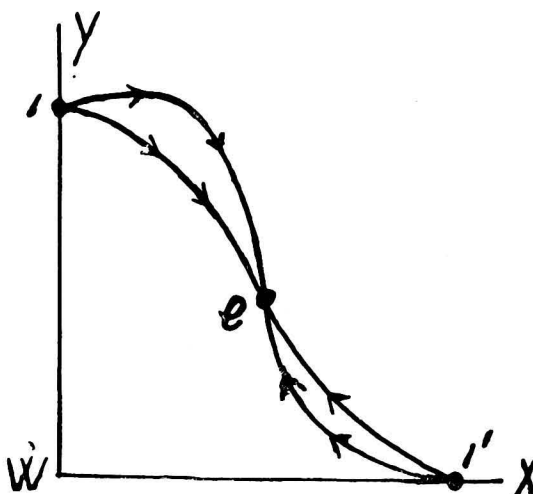

Fig. 2.   Fig. 3.

We are also able to show that those paths must touch one another in their starting points 1 and $1'$.

The rate at which the different substances diffuse through the membrane and consequently also the ratio in which this takes place at every moment, is also dependent on the nature of the membrane; therefore, this also defines the form of the osmosis-path.

Let us take as example an osmotic system

$$L_1 \mid L_1' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which L_1 only contains the substances W and Y and the liquid L_1' only the substances W and X. Then the liquid L_1 is represented in fig. 3 (in which the sides WX and WY of the concentration-triangle are only partly drawn) by a point 1 on the side WY; the liquid $1'$ is indicated by a point $1'$ on the side WX. As soon as the diffusion of the substances through the membrane has begun, each of the liquids contains three substances; they are represented by points within the triangle.

It now depends on the kind of membrane along which paths the liquids will travel; in fig. 3 two osmosis-paths are drawn; we have defined them in the system:

$$W = water \qquad X = Na_2S_2O_6 \qquad Y = BaS_2O_6.$$

Consequently the liquid L_1 contained: water $+ \; BaS_2O_6$ and the liquid L_1': water $+ \; Na_2S_2O_6$.

2. *The experimental osmosis-path.*

We shall call the osmosis-path, discussed above, the "theoretical" osmosis-path of a system. In order to define this path experimentally, we have to take away, however, now and then a small quantity of the two liquids in order to analyse them. We shall show that the system now no longer travels along the theoretical path, but along a path, more or less modified, which we shall call the "experimental".

We take two liquids L_1 and L'_1 the composition of which is known; if we bring n_1 quantities of L_1 on the one side and n'_1 quantities L'_1 on the other side of the membrane, then we have the osmotic system:

$$n_1 \times L_1 \mid n'_1 \times L'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

We represent the two liquids L_1 and L'_1 and the final-liquid L_e in fig. 1 by the points 1, 1' and e; as yet we eliminate the osmosis-path and its conjugation-lines from the figure.

After a certain time system (10) has passed into the still unknown system:

$$n_2 \times L_2 \mid n'_2 \times L'_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In order to learn the composition of the liquids we take away a small quantity of the liquids on both sides of the membrane and we determine their compositions; we represent it in fig. 1 by the points 2 and 2'; of course the conjugation-line passes through the point e. During the osmosis the liquids have now gone along the theoretical path 1.2 and 1'.2', of which, however, only the points 1, 2, 1' and 2' are known.

As we have taken away a little of the liquids L_2 and L'_2, we have no longer the system (11) which has arisen from (10) but a new system:

$$(n_2 - q_2) \times L_2 \mid (n'_2 - q'_2) \times L'_2 \quad . \quad . \quad . \quad . \quad (12)$$

in which q_2 and q'_2 are the quantities taken away; consequently the systems (11) and (12) consist of the same liquids, but the quantities of those liquids are different.

Above (comp. fig. 2) we have seen already that the osmosis-path of a system depends not only on the composition of the two liquids, but also on the quantities which are present on both sides of the membrane. System (11) which, however, we have no more, would therefore travel along a path differing slightly from system (12) which we do have.

When system (12) has passed after some time into the system:

$$n_3 \times L_3 \mid n'_3 \times L'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

then we are able to ascertain again the composition of both the liquids; we imagine them to be represented by the points 3 and 3'. The liquids have travelled now along the paths 2.3 and 2'.3'; they are the theo-

retical paths of system (12) and, therefore, not those of the original system. Consequently the curves 1.2 and 2.3 are parts of several theoretical paths; so their prolongations do not coincide. It follows, however, from our previous considerations that both paths touch one another in point 2, so that in this point not a discontinuous transition but a continuous transition takes place.

In the same way it follows that the theoretical path 3.4 is again somewhat different from the theoretical path 2.3; etc.

The difference between the two paths 1.2 and 2.3 in the point 2 depends on the difference, between the two ratios:

$$n_2 : n_2' \text{ and } (n_2 - q_2) : (n_2' - q_2') \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The less those ratios differ, the less also the paths 1.2 and 2.3 differ. If on both sides of the membrane we take away quantities q_2 and q_2' which are small with respect to the present quantities n_2 and n_2' then the both ratios (14) are equal approximately and the theoretical path 2.3 is also equal approximately to the theoretical path 1.2.

If on both sides of the membrane we take away an equal part of the liquids, then we have:

$$q_2 : q_2' = n_2 : n_2'$$

both ratios (14) have now become equal and the paths, 1.2 and 2.3 now form the same theoretical path. Consequently we may say:

the experimental osmosis-path consists of a succession of parts of theoretical paths, which pass into one another in the points, experimentally defined; this transition takes place continuously. The less their ratio is changed when a small quantity of the liquids is taken away, the less those theoretical paths differ from each other.

Above we have seen that the conjugation-lines of a theoretical path intersect one another all at the same point, consequently all conjugation-lines of points of the path 1.2 with points of the path 1'.2' go through point e. All conjugation-lines of points of the path 2.3 with points of the path 2'.3', therefore, go also through a same point; this, however, is not the point e but another point, not indicated in the figure, on the line 2.2' which we shall call h.

Previously we have seen that the position of point e on the line 2.2' is defined by:

$$e.2 : e.2' = n_2' : n_2$$

The position of point h on the line 2.2' is defined by:

$$h.2 : h.2' = (n_2' - q_2') : (n_2 - q_2)$$

This shows that the ratios, which define the difference in the position of the points e and h are the same as the ratios (14), which define the difference of the two theoretical paths 1.2 and 2.3. Just as the theoretical paths themselves, consequently also the points e and h will coincide

the more, the less we change their ratio on taking away a little of the liquids.

It appears from the previous considerations that it is possible to define experimental paths, which practically coincide with the theoretical. For this reason we shall first start from the theoretical paths in our following considerations.

(To be continued).

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