Chemistry. — *On absorption and osmosis.* I. By F. A. H. SCHREINEMAKERS and C. L. DE VRIES.

(Communicated at the meeting of February 25, 1933).

I. *Introduction.*

If we bring a membrane into a liquid, it will absorb all the substances from it, for which this membrane is permeable. Generally this membrane can and will change its nature and consequently also its absorption-capacity during the absorption under the influence of all sorts of factors (the action of the substances absorbed, hysteresis, etc.); we shall refer to this later on, when discussing the experimental investigations and for the sake of simplicity we now shall begin by assuming that the membrane is invariant. namely that the factors mentioned are not active, at least not during the time that we are considering this membrane. If we now bring such an invariant membrane into a liquid L of a definite composition, it will get in it a definite amount of each of the substances absorbed.

We now bring a membrane M, capable of absorbing the substances W (water) and X, into a liquid z, consisting of W and X. If we represent the different substances, of which this membrane consists before it has absorbed other substances, by a single letter Q, then we may after the absorption represent this membrane M by

$$1\, gr\, Q + w\, gr\, W + x\, gr\, X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

namely by the number of grams of W and X, absorbed by 1 gr. of Q. Now we shall call w the W-amount and x the X-amount of this membrane.

We now imagine liquid z in fig. 1 represented in the well-known way by point z of line WX. We represent the W-amount of the membrane by the length of line zz' and the X-amount by the length of line zz''.

Now we begin by assuming that the substance X is a liquid, miscible with water in all proportions; then two liquids cannot be in equilibrium with one another, as is indeed the case e. g. in a system with water and aether, or water and anilin, etc. We then can give any composition to liquid z starting from pure water until the pure substance X; then point z proceeds along line WX (fig. 1), point z' along a curve $W'\, z'\, X$ and point z'' along a curve $W z''\, X''$; we call $W'\, z'\, X$ the W-curve and $W z''\, X''$ the X-curve of this membrane. This X-curve has been dotted in fig. 1 (and fig. 3).

In pure water this membrane gets a W-amount $= W\,W'$ and an X-amount, which is of course zero; in liquid q a W-amount $= qq'$ and an X-amount $= qq''$; in the pure liquid X a W-amount, which is of course zero, and an X-amount $= XX''$.

The W- and the X-curve of a membrane may have different shapes [1]). In fig. 1 the W-curve is a curve, descending from left to right; consequently the W-amount of the membrane will decrease in the same degree as the solution will get a greater X-amount. In fig. 2, in which

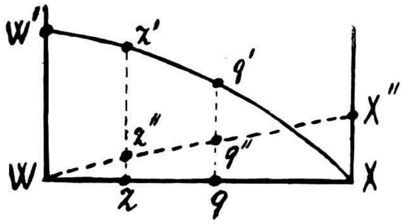

Fig. 1.

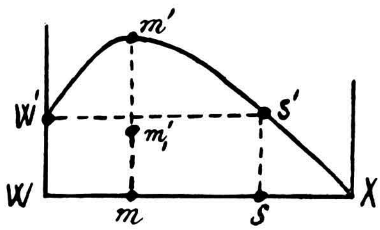

Fig. 2.

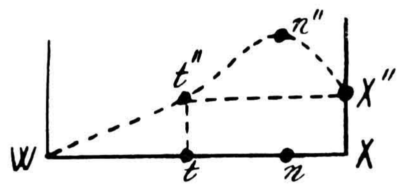

Fig. 3.

only a W-curve has been drawn, this curve has a maximum in m'. If we first bring this membrane into pure water and then add the substance X, the W-amount of this membrane will first increase until it reaches a maximum mm' and will decrease afterwards. So this membrane gets in liquid s the same, in diluted solutions (namely between W and s) a greater and in concentrated solutions (namely between s and X) a smaller W-amount than in pure water.

In fig. 1 the X-curve is a curve ascending from left to right; so the X-amount of the membrane will increase in the same degree as the solution will get a greater X-amount. In fig. 3 in which only an X-curve has been drawn, this curve has a maximum in point n''. What has been said for the W-amount of a membrane in fig. 2 now obtains for the X-amount of the membrane.

Above we have assumed that X is a liquid. If, however, X is a solid substance, forming no hydrate, one of the liquids of line WX will be saturated with this solid X. If we represent this solution by q in fig. 1,

[1]) F. A. H. SCHREINEMAKERS, These Proceedings **32**, 837 (1929); Rec. Trav. Chim. Pays-Bas **50**, 883 (1931).

then the points between W and q represent unsaturated solutions and the points between q and X supersaturated and, therefore, metastable solutions. If we now limit ourselves to the absorption in stable solutions, we may leave the parts of the W- and X-curve, situated on the right side of the line $q\,q''\,q'$ out of consideration.

When X is a solid substance, which can also form one or more hydrates, then several solutions can be saturated with a solid substance. In connection with the experimental determinations, to be discussed later on, we shall take here only the simplest case, namely that there is only one saturated solution, viz. with a hydrate $X.n\ H_2O$. If we now imagine that q (fig. 1) represents this saturated solution, the same rules as we have quoted above, obtain for the liquids between W and q and between q and X and for the parts of the W- and X-curves situated on the right side of the line $q\,q''\,q'$.

Of course the same obtains also for the figs 2 and 3, in which this point q has not been drawn.

Above we have represented the composition of the membrane after the absorption by:

$$1\ gr\ Q + w\ gr\ W + x\ gr\ X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

namely by the number of grams of W and X, which have been absorbed by one gram of the dry substance Q. We may also represent this composition by:

$$(1 - w_1 - x_1)\ gr\ Q + w_1\ gr\ W + x_1\ gr\ X \quad . \quad . \quad . \quad . \quad (3)$$

This means that one gram of the humid membrane (viz. after the absorption) contains w_1 grams of W, x_1 grams of X and consequently $1 - w_1 - x_1$ grams of the dry substance Q. Now we may also call w_1 and x_1 the W- and the X-amount of this membrane and draw them in the figs 1—3; then we shall call these absorption-curves the W_1- and the X_1-curve to distinguish them from the others.

It is clear now that this W_1- and this X_1-curve of a membrane will have an other shape and position than its W- and X-curves; we are able to deduce this in the following way.

From (2) it follows that $1 + w + x$ grs of the humid membrane contain w grs of W and x grs of X; consequently one gram of this membrane contains $w : (1 + w + x)$ grs of W and $x : (1 + w + x)$ grs of X. From this follows for w_1 and x_1 of (3):

$$w_1 = \frac{w}{1 + w + x} \quad \text{and} \quad x_1 = \frac{x}{1 + w + x} \quad . \quad . \quad . \quad . \quad (4)$$

From this it follows $w_1 < w$ and $x_1 < x$ so that the W_1- and the

X_1-curve must always be situated of course lower than the W- and the X-curve, except in the points X and W.

If we represent the X-amount of a liquid of line WX (figs 1—3) by c, then w and x are functions of c; the same obtains for w_1 and x_1. If we now write (4) in the form:

$$(1 + w + x)\, w_1 = w \quad \text{and} \quad (1 + w + x)\, x_1 = x \quad . \quad . \quad . \quad (5)$$

we find:

$$(1 + w + x) \frac{dw_1}{dc} = (1 - w_1) \frac{dw}{dc} - w_1 \frac{dx}{dc} \quad . \quad . \quad . \quad . \quad (6)$$

$$(1 + w + x) \frac{dx_1}{dc} = - x_1 \frac{dw}{dc} + (1 - x_1) \frac{dx}{dc} \quad . \quad . \quad . \quad . \quad (7)$$

in which, as appears from (3), $1-w_1$ and $1-x_1$ are positive.

When the W- and the X-curve have a shape as in fig. 1, then in each point of these curves:

$$\frac{dw}{dc} < 0 \quad \text{and} \quad \frac{dx}{dc} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From (6) and (7) now follows for every point of the W_1- and the X_1-curve:

$$\frac{dw_1}{dc} < 0 \quad \text{and} \quad \frac{dx_1}{dc} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From this it follows that the W_1- and the X_1-curve will have a shape as in fig. 1, namely that these curves will have neither a maximum nor a minimum.

We now assume that the W-curve has a shape like that in fig. 2 and the X-curve like that in fig. 1. In fig. 2 we shall represent the point of intersection of the W_1-curve with the line mm' by point m'_1, which must be situated below m', as we have seen before.

As for part $m'X$ of the W-curve the same rules obtain again as mentioned in (8), part m'_1X of the W_1-curve will also descend from left to right.

In point m' of the W-curve $\frac{dw}{dc} = 0$; as $\frac{dx}{dc} > 0$, it follows from (6) $\frac{dw_1}{dc} < 0$. Consequently the W_1-curve has no maximum in point m'_1, but will descend in this point from left to right. It being yet possible, however, as we shall see presently, that the W_1-curve may have a maximum, this must be situated then on the left side of line mm'.

Following the W-curve starting from m' and going towards W^1, $\frac{dw}{dc}$, which is zero in m', will become positive. It now appears from (6), as we have indeed seen already before, that $\frac{dw_1}{dc}$ is negative in m'_1. As however, $\frac{dw}{dc}$ becomes positive on the left side of m', $\frac{dw_1}{dc}$, as follows from (6) can remain negative or become positive at some distance from point m'_1. In the first case the W_1-curve will continue its ascent starting from m'_1, and going towards the left; in the second case this curve will first continue its ascent, starting from m'_1 towards the left, then pass through a maximum and descend afterwards. Consequently we find:

when the W-curve has a shape as the one in fig. 2 and the X-curve a shape like that in fig. 1, the W_1-curve may have a shape either as like that in fig. 1 or like that in fig. 2; in the latter case the maximum of the W_1-curve is situated, however, on the left side of that of the W-curve, namely on the left side of line mm'.

From these considerations, which the reader may also apply to the other cases, it appears that, in looking for a possible connection between the osmosis through a membrane and the shapes of its absorption-curves, we have to pay attention to the way in which its W-and its X-amount have been represented.

Until now we have assumed that the membrane is invariant, namely that its state does not change; for this reason we shall call the absorption-curves discussed above "1. state curves".

Membranes like e.g. cellophane, pig's bladder, etc. consist, however, of colloïdal substances, the properties of which change continuously under the influence of all sort of factors (the after-effect of states formerly passed through, the action of the substances absorbed, irreversible changes and fluctuations of temperature or pressure, etc.). These changes may continue till the membrane has lost its colloidal properties. We shall call such a membrane the state of which varies [1]) a "variant" membrane.

If we now bring such a membrane into a liquid, consisting of W and X, then experience has taught us that this will get a W- and an X-amount, which after $\pm$ 25 minutes usually change, but slowly; we shall call this the "practical" W- and X-amounts of this membrane.

It appeared among other things from the following experiment that this slow change in the absorption can go on a long time [2]). A pig's bladder of 0.808 grs. was brought into a solution of 3 % Na_2CO_3; from quite a series of determinations we only mention that this bladder after 2 days had absorbed 2.725 grs, after 4 days 2.830 grams and

[1]) F. A. H. SCHREINEMAKERS. Rec. Trav. Chim. Pays-Bas **50** 883 (1931).

[2]) J. P. WERRE and H. H. SCHREINEMACHERS; comp. C. L. DE VRIES, Diss. Leiden 1932.

after 125 days 4.597 grams (of water + Na_2CO_3). A corresponding change occurred also when a bladder was brought into a solution of 6 % and into a solution of 9 % of Na_2CO_3. (l.c.).

We can also draw a diagram of the practical *W*- and *X*-amounts, a variable membrane gets in a liquid. (figs 1—3). We now can bring this membrane successively into different liquids *a*, *b*, *c* etc. and determine its practical *W*- and *X*-amounts every time; if we draw them in the diagram and if we draw two curves through them, we shall call these the practical *W*- and *X*-curves.

It is clear, however, that this membrane has a different prehistory in liq. *b* than it had in *a*; for then it has become older, it has undergone the action of liquid *a*, whether it is reversible or not, and the manipulations necessary in order to determine its absorption, etc. So in liquid *b* the membrane will have a state different from the one it had in liquid *a*; in liquid *c* it will have a state different again from the one in *b* and this obtains for every successive liquid, into which the membrane is brought. So in this way we do not determine anything but the practical *W*- and *X*-amounts of a membrane changing continuously. For this reason we may call the practical *W*- and *X*-curves "*n*-states curves".

Now it is clear that shape and position of these *n*-states curves will be dependent on all sorts of factors, only one of which we shall discuss.

Let us assume that we determine these *W*- and *X*-curves of a membrane, by bringing it successively e.g. into seven different liquids, which we shall call 1, 2 .... and 7. We now may change the sequence of the liquids, into which the membrane is brought successively, in a great many ways. Every change in this sequence will have an influence on the shape and position of the *W*- and *X*-curves.

If we take the liquids in a definite sequence e.g. 1, 2 .... 7 and if we repeat these determinations a second time, still taking these liquids again in the same sequence, then the *W*- and *X*-curves of this second series will differ from those of the first series; the same obtains for every new series of determinations.

If we sum up the influences discussed above and others under the name "prehistory" of the membrane, then we may say:

shape and position of the *n*-states-curves of a membrane depend upon its prehistory.

II. *The absorption of water and sodium-carbonate by a pig's bladder* [1]).

Of the many series of absorption-determinations of water and sodium-carbonate by a pig's bladder, we shall here discuss only a few.

For the determination of the absorption, to be discussed here, five

[1]) C. L. DE VRIES. Dissertation Leiden 1932.

liquids were used, the composition of which is found in table A; from this it appears that liquid N°. 1 consisted of pure water and that N°. 5 contained 11°/₀ of Na_2CO_3.

Successively three bladders were now brought into the liquids N°. 1, 2.... and 5 at 25°; their practical *W*- and Na_2CO_3-amounts were determined after every three hours.

Afterwards these same bladders were brought again successively into the liquids No. 1, 2.... and 5, their practical *W*- and Na_2CO_3-amount being determined again and again; afterwards these determinations were repeated still a third and fourth time, the bladders being put again into the five liquids in the same order; at last these bladders were once more brought into liquid 1, viz. in pure water. For the sake of simplicity we now shall call the determinations during which a bladder is put successively into a series of liquids: "a period".

TABLE A.

	N°. 1	N°. 2	N°. 3	N°. 4	N°. 5
°/₀ Na_2CO_3	0	2	5	9	11
°/₀ Water	100	98	95	91	89

The results of these determinations with respect to one of these bladders are found in table 1 and 2. In table 1 we find the number of

TABLE 1
gr. Water absorbed by 1 gr. of the pig's bladder.

	N°. 1	N°. 2	N°. 3	N°. 4	N°. 5
1st period →	2 12	3.45	2.19	1.42	1.05
2nd „ →	3.45	3.51	2.52	1.66	1.21
3rd „ →	4.28	3.53	2.33	1.61	1.32
4th „ →	4.25	3.47	2.49	1.67	1.34
5th „ →	4.07	—	—	—	—

grams of water and in table 2 the number of grams of Na_2CO_3 which have been absorbed in the different periods by 1 gr. of the bladder. The arrows indicate the direction, in which the bladder was passed through these liquids; we see that they agree with what was discussed above.

From table 1 it appears that in the first period 1 gr. of this bladder absorbs 2,12 grs from liquid No. 1 (pure water); 3,45 grs from liq. No. 2 (2 °/₀ Na_2CO_3); 2,19 grs of water from liquid No. 3 (5°/₀ Na_2CO_3),

TABLE 2

gr. $Na_2 CO_3$ absorbed by 1 gr. of the pig's bladder.

	N^0. 1	N^0. 2	N^0. 3	N^0. 4	N^0. 5
1st period →	0	0.076	0.112	0.122	0.112
2nd „ →	0	0.073	0.130	0.147	0.131
3rd „ →	0	0.074	0.124	0.156	0.152
4th „ →	0	0.077	0.131	0.158	0.157
5th „ →	0	—	—	—	—

etc. So the *W*-curve has a maximum in its first period and may be represented schematically by fig. 2.

From the second period of table 1 it appears that the prehistory of the bladder has a great influence on its *W*-absorption; the *W*-amount of this bladder, namely, is now in all liquids greater than in the first period. The *W*-curve of this second period still has a maximum indeed, but an other shape and other position than in the first period.

From the third period it appears that the bladder has once more changed its *W*-absorption; the same appears again also from the fourth period. In these two periods the *W*-curve has no maximum any more and may now be represented schematically by the *W*-curve of fig. 1.

It appears from table 2 that the prehistory of the bladder also has an influence on its *X*-absorption ($X = Na_2CO_3$). We see that in the *X*-curves of the periods 1, 2 and 3 a maximum is obviously present, in that of the fourth period, however, there is only a very faint maximum. So these *X*-curves may be represented schematically by fig. 3.

Three other bladders were now also passed successively through four periods in the liquids of table A. In the first and third periods these bladders were passed through the liquids No. 1, 2 and 5, in the second and fourth periods they were passed through these liquids in the opposite

TABLE 3

gr. Water absorbed by 1 gr. of the pig's bladder.

	N^0. 1	N^0. 2	N^0. 3	N^0. 4	N^0. 5	
1st period →	1.47	3.54	2.14	1.39	1.01	
	3.42	3.20	2.24	1.45	1.09	← 2nd period
3rd „ →	3.17	3.25	2.22	1.50	1.26	
	3.56	3.32	2.28	1.58	1.36	← 4th „

direction, namely in the order 5,4 ... and 1 (comp. the arrows in tables 3 and 4, which have been arranged in the same way as tables 1 and 2).

The results of these determinations with respect to one of these bladders are found in tables 3 and 4.

From these determinations it appears again that the prehistory of the bladder has a great influence on its W-absorption. The W-curves of

TABLE 4

gr. Water absorbed by 1 gr. of the pig's bladder.

	N⁰. 1	N⁰. 2	N⁰. 3	N⁰. 4	N⁰. 5	
1st period →	0	0.077	0.111	0.122	0.106	
	0	0.071	0.114	0.128	0.112	← 2nd period
3rd „ →	0	0.070	0.120	0.146	0.145	
	0	0.073	0.122	0.146	0.156	← 4th „

the first and third periods namely have a maximum, in those of the second and fourth periods this maximum has disappeared, however. The influence on the X-absorption is smaller but still obvious. The X-curves of the first and second periods obviously have a maximum, that of the third period only has a very faint maximum left, which has disappeared in the fourth period.

From the determinations discussed above and the great number of others in which a bladder was passed successively through 6 or 7 liquids in different order, it appears that the W- and X-amounts and consequently also the shape and the position of the W- and X-curves of a pig's bladder depend entirely on its prehistory.

III. *The absorption of water and succinic acid by pig's bladder.* [1])

In order to determine the absorption of water and succinic acid six liquids were used, which we shall call No. 1, 2 ... and 6, liquid No. 1 consisted of pure water.

Three pig's bladders were passed through these liquids in the order N⁰. 1, 2 .... 6 and 1 and three other bladders were passed through these liquids in the opposite direction, namely in the order 1, 6, 5 .... and 1; each of the six X-curves now still had a shape as in fig. 1; each of the three W-curves, however, now had a shape as in fig. 2, namely with a maximum.

The period, passed through by each of the six bladders, began and

[1]) C. L. DE VRIES l. c.

ended with liq. N⁰. 1 namely with pure water; it now appeared that the *W*-amount of these bladders in pure water at the end of the period was much greater than at the beginning (e.g. 5.39 and 1.13).

From the above it appears that the prehistory of the bladder also has a great influence on its absorption in this system.

IV. *The absorption of water and tartaric acid by pig's bladder* [1]).

In order to determine the absorption of water and tart. acid thirteen bladders were used, which were passed through the liquids of one or more periods in the same or in a different order. Although all *W*-curves could be represented schematically by fig. 2 and all *X*-curves schematically by fig. 1, these determinations again showed quite clearly the great influence of the prehistory of the bladder on its absorption.

V. The absorption of water and tartaric acid by cellophane [2]).

To determine the absorption seven bladders were used, each of which was passed successively through different periods of seven liquids. All *W*- and *X*-curves showed a shape as in the schematical fig. 1. The influence of the prehistory of the cellophane was also clearly perceptible here; this influence acted on the cellophane in other direction than on the bladder of the preceding system.

(To be continued).

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Embryologie. — *Über den Glykogenstoffwechsel des Organisationszentrums in der Amphibiengastrula.* Von M. W. WOERDEMAN.

(Communicated at the meeting of February 25, 1933.)

Die Entwicklungsmechanik hat uns mit ausserordentlich wichtigen Erscheinungen bekannt gemacht, die während der Gastrulation des Amphibieneies auftreten und das Thema der schönen Untersuchungen von SPEMANN und seinen Mitarbeitern gebildet haben.

Es hat sich herausgestellt, dasz während der Gastrulation die Determination stattfindet und dasz diese Determination von der dorsalen Urmundlippe ausgeht („Organisationszentrum"). Auch wurde gefunden, dasz vom Urmunddach Induktionswirkungen ausgehen, wodurch das Ektoderm, womit es in Berührung tritt, zur Bildung einer Neuralplatte veranlasst wird.