Chemistry. — *Membrane and Osmosis*. I. By F. A. H. SCHREINEMAKERS.

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Introduction.

In previous communications [1]) we have described the phenomena obtaining with the osmosis of one or more substances, with the aid of the O. A. (Osmotic-Attraction) of the two liquids; follows the question whether these phenomena may also be explained with the aid of the absorption of the membrane; before discussing this question however, we shall first enter upon a brief survey of this absorption.

We represent the various substances of which a membrane consists, before it has absorbed any other substances, by a single letter Q. If we have a membrane $M(W)$ i.e. a membrane absorbing water only, its composition, when this membrane will have absorbed water, may be represented by:

$$1\ gr\ Q + w\ mol\ (gr)\ W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

i.e. by the number of mols (or grams) of water absorbed by 1 gr. of Q; we shall call w the W-amount of this membrane.

If this dry membrane is put into a liquid from which it takes water, its W-amount will first increase more rapidly and later on more slowly, until it will finally change no more and the membrane is saturated with water (we shall refer to this later on). We then have a system:

$$L + M(W) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the two phases are in equilibrium; with every composition of liquid L then goes a definite W-amount of the membrane; in order to enable us to describe some phenomena later on in a more simple way, we shall say that liquid L gives this W-amount to the membrane, or that the membrane obtains this W-amount in the liquid L.

Binary liquids and a membrane $M(W)$.

In system (2) we now take for L a binary liquid, containing the substances $W + X$; we represent this in the usual way by a point of line WX (figs. 1—4).

[1]) Verslagen Kon. Akademie Amsterdam, **36**, 779, 987, 1103, 1218 (1927); **37**, 374, 634, 849 (1928).

These Proceedings, **30**, 761, 934, 1095, 1106 (1927); **31**, 459, 811, 923 (1928); **32**, 23, 254 (1929).

We now represent the W-amount given to the membrane by a liquid a_1, by point w_1 i.e. by the length of the line a_1w_1, intersecting WX perpendicularly.

We now imagine that the liquid gets every possible composition, so that it will be represented successively by all points of WX; as a definite W-amount goes with every liquid, the point representing this W-amount will travel along a curve; we shall call it the W-curve of the membrane. We may imagine this to be represented in figs. 1 and 3 by the fully-drawn curve $W'X$.

Point w_2 (viz. the length of line a_2w_2) consequently represents the W-amount given to the membrane by liquid a_2; point W' represents the W-amount the membrane gets in pure water; etc. Point X represents a liquid consisting of substance X only; as consequently the membrane cannot absorb water here either and its W-amount must therefore be zero, the W-curve must also run through point X.

If the composition of the liquid in system (2) is changed, the membrane will generally also change its W-amount; we now may deduce:

A_1. if water is added to the liquid, the membrane $M(W)$ will also absorb water; consequently its W-amount will increase;

A_2. if water is taken from the liquid, the membrane $M(W)$ will also give out water; so its W-amount will become smaller.

As we shall see later on, however, this obtains only for a membrane $M(W)$; for it does not obtain any longer, as soon as the membrane, besides water, absorbs one or more other substances too.

We now apply this to liquid a_1 of fig. 1. When water is added, this liquid will travel along line a_1W, starting from a_1 going to W; so the W-amount of the membrane must increase from w_1 as far as point W'. If water is taken from liquid a_1, this liquid will travel along line a_1X from a_1 to X; then the W-amount of the membrane must decrease from w_1 as far as X. So the W-curve must descend continually from point W as far as point X. We shall call such a curve, showing neither a maximum nor a minimum "monotonous". Then we may say:

B. the W-curve of a membrane $M(W)$ is a monotonous curve.

When deducing the W-curve we have assumed that X is a liquid; if X is a solid, however, one of the liquids will be saturated with solid X. If this should be the liquid a_2 for instance, w_2 will represent the W-amount the membrane will get in the liquid saturated with X; part w_2X of the W-curve will then represent metastable conditions, viz. the W-amount the membrane would get in supersaturated liquids.

It would also be possible to imagine a hydrate of X occurring as a solid, or an unmixing in two liquids; it does not serve our purpose, however, to discuss this here.

Binary liquids and a membrane $M(X)$.

Every thing that has been said above of a membrane $M(W)$ obtains for any other membrane absorbing one substance only. If we have e.g. the system:

$$L + M(X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the membrane absorbs only the substance X, we may represent the composition of the membrane by:

$$1\ gr\ Q + x\ mol\ X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Instead of A_1 and A_2 we now have:

C_1. when X is added to the liquid, the membrane $M(X)$ will also absorb X;

C_2. if X is taken from the liquid, the membrane $M(X)$ will also give out X.

Instead of B we have:

D. the X-curve of a membrane $M(X)$ is a monotonous curve.

We may imagine this X-curve to be represented in figs. 1 and 2 by the dotted curve WX'; so the membrane will get an X-amount $= a_1x_1$ in the liquid a_1, an X-amount $= a_2x_2$ in the liquid a_2; etc.

Binary liquids and a membrane $M(n)$.

We now take a system:

$$L + M(n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which the membrane absorbs the two substances W and X; we may then represent the composition of this membrane by:

$$1\ gr\ Q + w\ mol\ W + x\ mol\ X \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If for instance the membrane is put into the liquid a_1 (figs. 1—4) we get a definite W- and X-amount in it; we once more represent this W-amount by a point w_1 and the X-amount by a point x_1.

If we now suppose that the liquid travels along line WX, we get two curves; we shall call them the W- and the X-curve of the membrane $M(n)$.

So the membrane $M(n)$ has a W- as well as an X-curve, whereas a membrane $M(W)$ has a W-curve only, and a membrane $M(X)$ an X-curve only. The W- and X-curves of a membrane $M(n)$ however, are different curves and may have a shape differing greatly from that of the W-curve of a membrane $M(W)$ and the X-curve of a membrane $M(X)$. These two curves namely, are always monotonous, as has already been stated in B and D; this does not always obtain any longer however for the W- and X-curves of a membrane $M(n)$. We now may distinguish the following cases:

E_1. both curves are monotonous (fig. 1);

E_2. the W-curve has a maximum; the X-curve is monotonous (fig. 2);

E_3. the W-curve is monotonous; the X-curve has a maximum (fig. 3);

E_4. both curves have a maximum (fig. 4);

E_5. in one curve or in both curves we find besides a maximum also a minimum.

-If we have a membrane for which E_1 obtains, we may imagine the W- and X-curves to be represented by fig. 1. The shape of these curves shows :

if more and more of the substance X is continually added to the water, the W-amount of the membrane will decrease and its X-amount increase continually.

In our next paper we shall discuss an example.

If we have a membrane, for which E_2 obtains, fig. 2 may represent the W- and the X-curve ; the W-curve here has a maximum in H_w.

If we suppose $a_4 w_4 = WW'$, the membrane will get the same

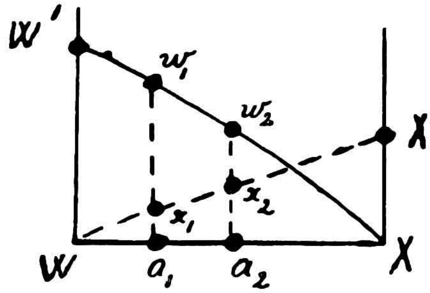

Fig. 1.

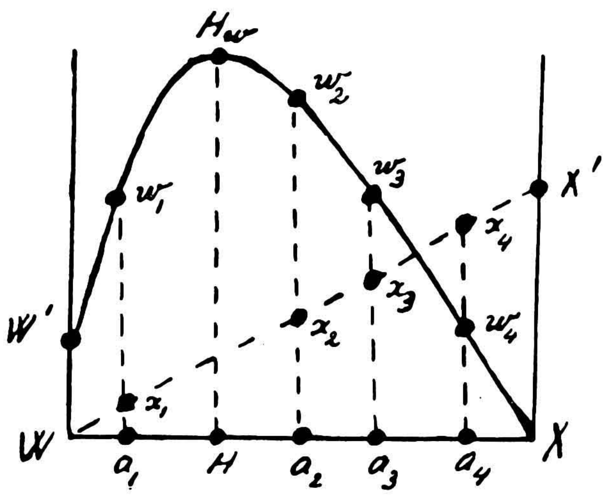

Fig. 2.

W-amount in the liquid a_4 as in pure water ; all liquids situated between W and a_4 give a larger-, all liquids situated between a_4 and X a smaller W-amount to the membrane than the pure water ; the liquid H gives the largest W-amount to the membrane. This shows :

if more and more X is continually added to the water, the W-amount of the membrane will begin by increasing, will reach a maximum, and decrease afterwards ; its X-amount will increase continually.

In our next paper we shall discuss an example.

Fig. 3 represents the W- and X-curves of a membrane, for which E_3 obtains ; the X-curve here has a maximum in the point U_x. We now see :

if more and more X is continually added to the water, the W-amount of the membrane will continually decrease ; its X-amount will begin by increasing, reach a maximum and decrease afterwards.

We now take a membrane, for which E_4 obtains ; both curves then have a maximum ; this has been represented in fig. 4. The two maxima

H_w and U_x cannot be situated arbitrarily with respect to each other; for if a liquid travels along line WX from W to X, the W-curve will be the

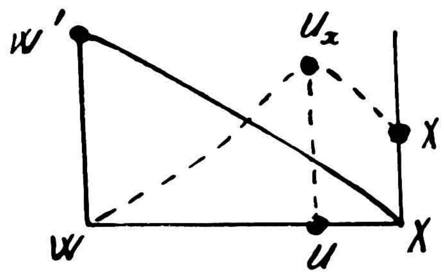

Fig. 3.

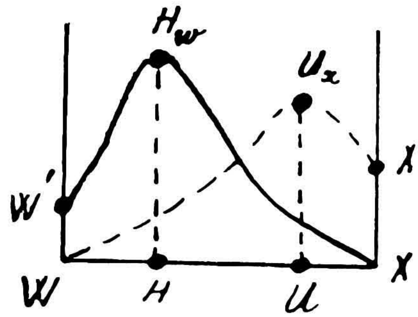

Fig. 4.

first to reach its maximum, followed by the X-curve. So when the membrane reaches its maximum W-amount, its X-amount will go on increasing; when it reaches its maximum X-amount, its W-amount will consequently decrease.

In our next paper we shall discuss an example.

If we have a membrane for which E_5 obtains, a minimum will occur in one curve or in both curves; it is clear that no minimum is possible without a maximum; we are not going to enter upon a discussion of this subject here.

Perhaps we might be inclined to believe now, that the W- and the X-curve may be situated quite arbitrarily with respect to one another, so that also the W- and the X-amount of the membrane might vary arbitrarily with respect to each other; this is not the case however.

To prove this we take an osmotic system:

$$n \times L + M \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

consisting of n quantities of a liquid L and of one quantity of a membrane. We shall call it system S. We represent the composition of L and M by:

$$x \, mol \, X + (1 - x) \, mol \, W \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

$$1 \; gr \; Q + x_0 \, mol \, X + w_0 \, mol \, W \quad . \; . \; . \; . \; . \quad (9)$$

We may now represent the total composition of this system S by:

$$1 \; gr \; Q + (nx + x_0) \, mol \, X + [n(1 - x) + w_0] \, mol \, W \quad . \; . \quad (10)$$

We now take a second system:

$$(n + dn) \times L' + M' \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

which we shall call S'. We suppose there is only a minute difference between L' and M' and L and M of system S; we may represent the composition of L' and M' by:

$$(x + dx)\, mol\, X + (1 - x - dx)\, mol\, W \quad . \quad . \quad . \quad . \quad (12)$$

$$1 \; gr \;\; Q + (x_0 + dx_0)\, mol\, X + (w_0 + dw_0)\, mol\, W \; . \quad . \quad . \quad (13)$$

in which dx, dx_0 and dw_0 are very small; dw_0 then is the change of the W-amount, dx_0 that of the X-amount of the membrane, when the X-amount of the liquid changes with dx.

We now may represent the total composition of this system S' by:

$$\left.\begin{array}{l} 1 \; gr \;\; Q + [(n + dn)(x + dx) + x_0 + dx_0]\, mol\, X + \\ \quad + [(n + dn)(1 - x - dx) + w_0 + dw_0]\, mol\, W \end{array}\right\} \; . \quad (14)$$

We now have the well-known theorem:

if two systems have the same total compositions, so that the one may change into the other, one of these systems is metastable or labile with respect to the other; the system having the smaller thermodynamical potential when temperature and pressure are constant, is the stabler of the two.

If we now suppose the W- and the X-curve to represent systems, stable with respect to each other, it must not be possible for the systems S and S' to change into each other; the total compositions of the two systems consequently must be different. Follows that the two equations:

$$nx + x_0 = (n + dn)(x + dx) + x_0 + dx_0 \quad . \quad . \quad . \quad . \quad (15)$$

$$n(1 - x) + w_0 = (n + dn)(1 - x - dx) + w_0 + dw_0 \quad . \quad . \quad (16)$$

expressing that the systems S and S' have the same compositions, (compare 10 and 14) are not valid.

If $dn \, . \, dx$, which is infinitely small with respect to dn and dx, is neglected, we find:

$$0 = x\, dn + n\, dx + dx_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$0 = (1 - x)\, dn - n\, dx + dw_0 \quad . \quad . \quad . \quad . \quad . \quad (18)$$

After elimination of dn follows:

$$n\, dx = x\, dw_0 - (1 - x)\, dx_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

To n in system S every possible value may be given between 0 and $+\infty$; if dx is taken positive, the same must obtain for ndx. So it will only then be impossible to satisfy (19) when the second term is always negative; so dw_0 and dx_0 must satisfy:

$$x\, dw_0 - (1 - x)\, dx_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

a relation we can also deduce in an other way. This makes it clear that the W- and X-amounts of a membrane cannot change arbitrarily; for these changes must satisfy (20).

If only the signs of dw_0 and dx_0 are heeded, we may imagine the four cases of table I; if besides we suppose $dw_0 = 0$, or $dx_0 = 0$, we may also imagine the four cases of table II. As however, dw_0 and dx_0 must satisfy (20) these cases will not all of them be possible.

TABLE I.

	dw_0	dx_0
a.	+	+ (cond.)
b.	—	+
c.	—	— (cond.)
d.	[+	—]

TABLE II.

	dw_0	dx_0
e.	0	+
f.	—	0
g.	[0	—]
h.	[+	0]

If for instance we suppose: $dw_0 =$ pos., it will only be possible to satisfy (20) by $dx_0 =$ pos. (case *a*); case *h*, viz. $dx_0 = 0$ and case *d*, viz. $dx_0 =$ neg. are impossible.

If we suppose $dw_0 = 0$, dx_0 must be pos. (case *e*); so case *g* viz. $dx_0 =$ neg. is impossible.

If we suppose $dw_0 =$ neg. (20) may be satisfied by $dx_0 =$ pos. (case *b*), by $dx_0 =$ neg. (case *c*) and by $dx_0 = 0$ (case *f*).

In table I we find with case *a* between brackets "cond." i.e. "condition"; the meaning of this is that *a* does not obtain for all arbitrary pos. values of dw_0 and dx_0, but only for those pos. values, satisfying a certain condition, viz. (20). The same obtains in *c* for the neg. values of dw_0 and dx_0.

We now write down (20) in this way:

$$\frac{dw_0}{dx} < \frac{1-x}{x} \cdot \frac{dx_0}{dx} \quad \ldots \ldots \ldots \quad (21)$$

Here dw_0/dx is the direction of the tangent in a point of the W-curve and dx_0/dx the direction of the tangent in the corresponding point of the X-curve. If we take e.g. the liquid a_1 (compare the preceding figures) dw_0/dx will determine the direction of the tangent in point w_1 of the W-curve and dx_0/dx the direction of the tangent in point x_1 of the X-curve.

If, as will always be our practice in future, we follow a curve to the right, we shall find: the W-curve rises when dw_0/dx is pos.; it falls when dw_0/dx is neg.; it has a horizontal tangent, when dw_0/dx is zero.

The direction of the X-curve of course, is determined in a similar way by dx_0/dx.

If we imagine a rising direction of a curve indicated by the sign ↑, a falling one by ↓ and a horizontal tangent by —, the eight cases of tables III and IV may be imagined. These tables follow at once from tables I and II; for it is clear that the signs ↑ and +, signs ↓ and — and signs — and o agree.

In fig. 1 only case *b* is found viz. an ever falling W- and a rising X-curve.

In fig. 2 *a*, *b* and the transition-case *e* are found. For all liquids between *W* and *H* namely, the two curves rise (case *a*) ; for all liquids between

TABLE III.

	W-curve	X-curve	
a.	↑	↑	(cond.
b.	↓	↑	
c.	↓	↓	(cond.)
d.	[↑	↓]	

TABLE IV.

	W-curve	X-curve
e.	——	↑
f.	↓	——
g.	[——	↓]
h.	[↑	——]

H and *X* the *W*-curve will fall, the X-curve rise (case *b*) : for liquid *H* the *W*-curve has a horizontal tangent and the *X*-curve will rise (case *e*).

In fig. 3 the cases *b*, *c* and the transition-case *f* are found ; in fig. 4 all cases are found these tables have shown to be possible.

Table IV proves that the *X*-curve must rise, when the *W*-curve has a maximum (case *e*), and that the *W*-curve must fall when the *X*-curve has a maximum ; figures 2, 3 and 4 agree with this. The cases *d*, *g* and *h* which have been shown to be impossible, do not occur in the figures.

(To be continued.)

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