

Chemistry. — *Osmosis in binary systems in which two membranes.* I. By
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We take an osmotic system :

$$\text{inv. } L_1 (W + X) \Big|_{\omega_1}^{M_1} L (x) \Big|_{\omega_2}^{M_2} \text{inv. } L_2 (W + X) \quad . \quad . \quad . \quad (1)$$

in which two membranes M_1 and M_2 with the surfaces ω_1 and ω_2 ; on the left side of M_1 and on the right side of M_2 is an invariant liquid, containing the substances W (water) and X . In order to concentrate our thoughts we assume that L_1 has a smaller X -amount than L_2 ; if in fig. 1 we represent L_1 and L_2 by the points i_1 and i_2 in the well-known way, then i_1 must be situated, therefore, on the left side of i_2 .

If we now bring a liquid L with an arbitrary composition

$$x \text{ quant. } X + (1 - x) \text{ quant. } W \quad . \quad . \quad . \quad . \quad (2)$$

between the two membranes this liquid will continue to change until a stationary state occurs, which we represent by :

$$\text{inv. } L_1 (W + X) \Big|_{\omega_1}^{M_1} \text{stat. } L (x) \Big|_{\omega_2}^{M_2} \text{inv. } L_2 (W + X) \quad . \quad . \quad . \quad (3)$$

The osmosis is not done then, however, for the substances W and X continue to pass all the time through the two membranes; this, however now takes place in such a way that the liquid L does not change its composition any more; the quantity of this liquid however generally does change still.

If we imagine the membrane M_2 of system (1) impermeable, then we have only to consider the system :

$$\text{inv. } L_1 (W + X) \Big|_{\omega_1}^{M_1} L (x) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We shall now assume that no stationary point occurs in this system so that the variable liquid L changes normally¹⁾; this means that during the osmosis this variable liquid in fig. 1 will always move towards point i_1 , no

¹⁾ Comp.: These Proceedings **34**, 1282 (1931).

Until now we have only found examples of a normal change in all systems investigated.

matter where this liquid L may be at the beginning of the osmosis. From this follows: if the variable liquid L is found in fig. 1 on the left side of i_1 then L will move \rightarrow ; if L is found on the right side of i_1 then L will move \leftarrow ; this has been indicated in fig. 1 by the three arrows of the top series.

If we imagine the membrane M_2 of system (1) impermeable, we get the system:

$$L(x) \Big|_{\omega_2}^{M_2} \text{inv. } L_2(W+X). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we now assume once more that in this system no stationary point will occur either, then we find that L will now move with respect to point i_2 as has been indicated in fig. 1 by the three arrows of the lowest series.

In system (1) the variant liquid L moves under the influence of the two invariant liquids. When L is found on Wi_1 , then the two influences coöperate to move $L \rightarrow$; when L is found on i_2X , then the two influences coöperate to move $L \leftarrow$.

When, however, L is found between i_1 and i_2 , the two influences work in opposite direction; as a matter of course we now assume that the two influences can now neutralise each other somewhere, so that liquid L will not move any more, but become stationary. Further on we shall see that this indeed happens and we shall deduce:

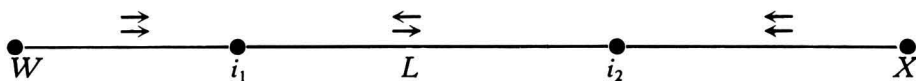


Fig. 1

in fig. 1 the stationary liquid is situated between i_1 and i_2 ; its place depends upon the ratio $\omega_1 : \omega_2$ of the two membranes.

For the directions in which the substances W and X flow through the membrane M_1 of system (4) we can imagine four $D.T.$'s, viz.:

$$\begin{array}{cc} X & W \\ 1. \leftarrow & \leftarrow \\ 2. \leftarrow & \rightarrow \end{array} \quad \begin{array}{cc} X & W \\ 3. \rightarrow & \leftarrow \\ 4. \rightarrow & \rightarrow \end{array} \quad \left. \vphantom{\begin{array}{cc} X & W \\ 1. \leftarrow & \leftarrow \\ 2. \leftarrow & \rightarrow \end{array}} \right\} . \quad . \quad . \quad . \quad . \quad (6)$$

of which one, namely the incongruent one, is not possible, however; when L has a greater X -amount than L_1 then $N^0. 3$ is incongruent; when, however, L has a smaller X -amount, $N^0. 2$ will be incongruent. Of course it depends upon the nature of the system, namely upon the nature and composition of the two liquids and the nature of the membrane, which of the three $D.T.$'s possible will occur. As during the osmosis liquid L continuously changes its composition, one $D.T.$ at a certain moment of the osmosis can pass into another.

In order to summarise the different cases, we represent the diffusion by :

$$\leftarrow a_1 \cdot X \quad \leftarrow \gamma_1 \cdot W \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which a_1 and γ_1 are the very small quantities of X and W , diffusing towards the left through 1 cM² of the membrane M_1 between the moments t and $t + dt$; if we take a_1 or γ_1 or both negative, then we get the other $D.T.$'s of (6).

As the membrane M_1 has a surface ω_1 , the variant liquid L gives off $\omega_1 a_1 X$ and $\omega_1 \gamma_1 W$ in the time dt . If we represent the quantity of this liquid at the moment t by m , then it is $m - \omega_1(a_1 + \gamma_1)$ at the moment $t + dt$. As this liquid now contains altogether $mx - \omega_1 a_1$ quantities of X , it follows :

$$(dx)_1 = \frac{mx - \omega_1 a_1}{m - \omega_1(a_1 + \gamma_1)} - x = -\frac{\omega_1}{m} [a_1 - x(a_1 + \gamma_1)]. \quad . \quad . \quad (8)$$

or :

$$m(dx)_1 = -\omega_1 A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which $(dx)_1$ represents the change in the X -amount of the var. liq. L .

Above we have seen : when liq. L of system (4) is on the left side of i_1 , it moves \rightarrow so that $(dx)_1 > 0$; when L is on the right side of i_1 , then L moves \leftarrow so that $(dx)_1 < 0$ [comp. the three arrows of the top series in fig. 1]. It now follows from (9) :

when the variant liquid L of system (4) is on the left side of i_1 , then $A_1 < 0$; when L is situated on the right side of i_1 , then $A_1 > 0$; when L is in i_1 , then $A_1 = 0$.

We find these signs of A_1 in the top series of fig. 2.

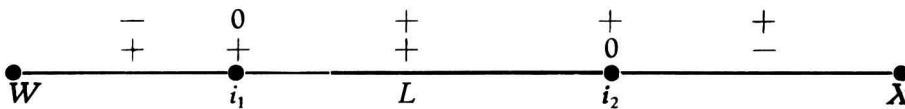


Fig. 2

Corresponding considerations also obtain for system (5). We now represent the diffusion by :

$$\leftarrow a_2 \cdot X \quad \leftarrow \gamma_2 \cdot W \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which a_2 and γ_2 indicate the very small quantities of X and W , now diffusing towards the left through 1 cM² of the membrane M_2 in the time dt . If we now represent the change in the X -amount of the variant liquid L by $(dx)_2$, we find :

$$(dx)_2 = \frac{\omega_2}{m} [a_2 - x(a_2 + \gamma_2)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or :

$$m(dx)_2 = \omega_2 A_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If we now take into consideration the direction in which the var. liq. moves with respect to point i_2 [compare the three arrows of the lower-series of fig. 1], then it follows that A_2 is positive on the left side of i_2 , negative on the right side of i_2 and zero in i_2 . We find these signs of A_2 in the lowest series of fig. 2.

If we represent by dx the change of the X -amount of the variable liquid L of system (1), then it follows from (9) and (12) :

$$mdx = m(dx)_1 + m(dx)_2 = \omega_2 A_2 - \omega_1 A_1 \quad . \quad . \quad . \quad (13)$$

If we take into consideration the quantities of X and W the var. liq. L absorbs through the membrane M_2 and gives off through M_1 , we see that

$$(\omega_2 a_2 - \omega_1 a_1) X \quad \text{and} \quad (\omega_2 \gamma_2 - \omega_1 \gamma_1) W \quad . \quad . \quad . \quad (14)$$

are absorbed by liquid L . So for the change dm in the quantity of this liquid follows :

$$dm = \omega_2 (a_2 + \gamma_2) - \omega_1 (a_1 + \gamma_1) \quad . \quad . \quad . \quad . \quad (15)$$

If we add (13) and (15) together, after having multiplied (15) by x and if we take into consideration the values of A_1 and A_2 , we find :

$$m dx + x dm = \omega_2 a_2 - \omega_1 a_1 \quad . \quad . \quad . \quad . \quad (16)$$

It is possible to find this relation (16) also directly ; the first part namely is $d(mx)$, consequently the increase of the total quantity of X in the liquid L ; the second part also represents this increase as is apparent from (14).

The relations mentioned above obtain for every arbitrary moment of the osmosis of system (1) ; when, however, the var. liq. L has passed into the stationary liquid of system (3), so that its composition does not change any more, $dx=0$. Then it follows from (13) that

$$\frac{\omega_2}{\omega_1} = \frac{A_1}{A_2} \quad \text{or} \quad \frac{\omega_2}{\omega_1} = \frac{a_1 - x(a_1 + \gamma_1)}{a_2 - x(a_2 + \gamma_2)} \quad . \quad . \quad . \quad (17)$$

must be satisfied, so that A_1 and A_2 must have the same sign.

We are able to deduce (17) in still another way. The var. liq. L namely will not change its composition any more, when the quantities of X and W absorbed or given off [comp. 14] stand in the relation of the X - and W -amount of this liquid L ; so

$$(\omega_2 a_2 - \omega_1 a_1) : (\omega_2 \gamma_2 - \omega_1 \gamma_1) = x : (1 - x) \quad . \quad . \quad . \quad (18)$$

must be satisfied, from which (17) follows ; in this way, however, we do not find, as we found above, what signs A_1 and A_2 have during the osmosis.

It appears from (17) that this condition can only be satisfied when A_1 and A_2 have the same sign ; as fig. 2 shows that this is only the

case between the points i_1 and i_2 , it follows as has been deduced already above, that the stationary liquid of system (3) can only be situated between i_1 and i_2 ; it now appears besides, however, that A_1 and A_2 in system (3) are positive then. We can also deduce now:

in system (3) a stat. liq. L always exists, no matter what surfaces the membranes M_1 and M_2 may have;

the composition of this stat. liq. depends upon $\omega_2 : \omega_1$ viz. on the ratio of the surfaces of the two membranes; if $\omega_2 : \omega_1$ is small, then L is situated close to point i_1 (figs. 1 or 2); if $\omega_2 : \omega_1$ is large, then L is situated close to point i_2 .

In order to deduce this we imagine the variable liquid L in fig. 2 moving from i_1 towards i_2 . With this movement A_1 then will increase from zero up to a certain positive value, whereas A_2 will decrease from a certain positive value to zero [comp. the signs in fig. 2]. From this it follows that the second part of (17) viz. $A_1 : A_2$ will run through all values from zero up to positive infinitely large. From this it follows:

(17) always can be satisfied, no matter what value $\omega_2 : \omega_1$ may have.

From this now follows at once what has been said above about the stat. liq. of system (3).

We now imagine in system (1) two membranes with definite surfaces ω_1 and ω_2 ; then the stat. liq. L of system (3) will have a definite composition; we imagine this liquid represented in figs. 3 and 4, in which line WX has only been partly drawn, by point s . Then the var. liq. L of system (1) will move towards this point (comp. the arrows in figs. 3 and 4) when namely it is not accidentally situated in point s at the beginning of the osmosis.

During this movement the variable liquid (as appears from 15) will be changing its quantity continuously, unless a point is situated in its way, where

$$\omega_2 (a_2 + \gamma_2) = \omega_1 (a_1 + \gamma_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

is satisfied, so that the quantity of the variable liquid does not change in this point; we shall call such a point "a point of constant quantity".

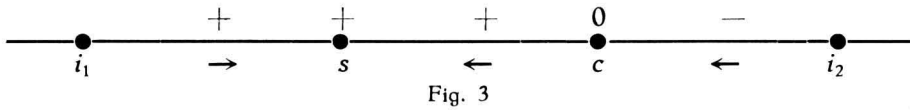
It depends upon the nature of the liquids and of the membranes whether a similar point will occur or not occur in a given system; we shall refer to this later on, when discussing some systems examined.

When system (1) has no point of constant quantity, the quantity of the var. liq. will either increase or decrease during the entire osmosis, no matter where the variant liquid may be found at the beginning of the osmosis; the quantity of the stationary liquid then will continuously increase or decrease as well.

When, however, a point of constant quantity does occur in the system, we can distinguish several cases. In order to discuss some of these cases

we imagine this point represented by point c in the figs. 3 and 4 ; in order to concentrate our thoughts we assume that the quantity of the variable liquid increases on the left side of this point c and decreases on the right side of c ; this has been indicated in the figs. 3 and 4 by the signs $+$ and $-$.

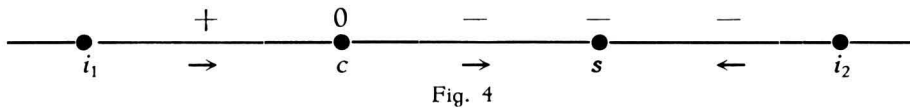
We now first take fig. 3. When at the beginning of the osmosis the



variable liquid is found between s and c , its quantity will increase during the entire osmosis and this process will still go on when the liquid has become stationary in point s .

When at the beginning of the osmosis the var. liq. is found on the right side of c , its quantity will first decrease, remain constant in point c for a moment and afterwards increase from c to s where the quantity also goes on increasing continuously. So during the osmosis the quantity of the var. liq. becomes a minimum in point c .

In fig. 4 point c is situated on the left side of point s . When at the



beginning of the osmosis the var. liquid is found between c and s or on the right side of s , its quantity will decrease during the entire osmosis and this will still go on when the liquid has become stationary in point s .

When at the beginning of the osmosis the var. liq. is found, however, on the left side of c , its quantity will first increase, remain constant in point c for a moment and afterwards it will decrease from c to s , where the quantity goes on decreasing continuously. Consequently during the osmosis the quantity of the variant liquid becomes a maximum in point c .

We may also imagine that the points c and s of figs. 3 or 4 coincide ; then $dm=0$ and $dx=0$ must be satisfied at the same time. With the aid of two of the three equations (13), (15) and (16) we find that (19) then must be satisfied and :

$$\omega_2 a_2 = \omega_1 a_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

or :

$$\frac{\omega_2}{\omega_1} = \frac{a_1}{a_2} \quad \text{and} \quad \frac{\omega_2}{\omega_1} = \frac{\gamma_1}{\gamma_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

If we now take a definite system, so that the invariant liquids L_1 and L_2 have a definite composition and the membranes a definite nature, then

α_1 , α_2 , γ_1 and γ_2 are functions, containing only the composition x of the var. liq. as a variable.

It now follows from (21) that not only x but also $\omega_2 : \omega_1$ must have a definite value. From this it appears that the points c and s of a given system can coincide only then when the ratio $\omega_2 : \omega_1$ of the surfaces of the two membranes has a definite value.

If we now have a system, in which the points c and s do not coincide, then, as we have seen before, we are able to make them coincide by changing the ratio $\omega_2 : \omega_1$ in such a way that (21) is satisfied; this is also possible, however, by giving an other composition to one or to both invariant liquids.

If we now represent the compositions of these inv. liquids by x_1 and x_2 , then α_1 and γ_1 will now be functions of x and x_1 , whereas α_2 and γ_2 are functions of x and x_2 ; as the equations (21) now contain three variables (viz. x_2 , x_1 and x) follows from this what has been said above.

From this it follows also that figs. 3 and 4 may pass into each other at the change in the composition of one or of both invariant liquids. We shall refer to this later on.

Above we have deduced: every arbitrary system (1) passes into a system (3), in which the stationary liquid L has a definite composition. In our further considerations we have assumed as a matter of course that only a single stat. liq. is possible; also other cases can be imagined, however.

Above we have seen: when in fig. 2 the variable liquid L of system (1) moves from i_1 towards i_2 , the second part of (17) [viz. the ratio $A_1 : A_2$] runs through all values from 0 to $+\infty$. We can imagine several cases here.

1^o. The value of $A_1 : A_2$ increases continuously. We then have the case, considered until now, that only a single stat. liquid belongs to every value of $\omega_2 : \omega_1$.

2^o. The value of $A_1 : A_2$ first increases from 0 to a certain value p , then it decreases to q and afterwards it increases continuously to ∞ . We now distinguish two cases.

a. If we take $\omega_2 : \omega_1$ greater than p or smaller than q , then only one single stat. liq. L belongs to every value of $\omega_2 : \omega_1$.

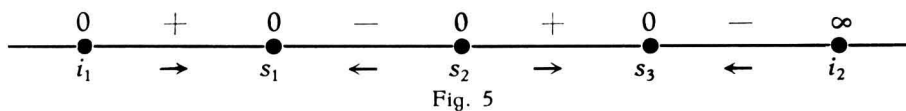
b. If we take $\omega_2 : \omega_1$ between p and q , then three quite different stat. liquids L belong to every value of $\omega_2 : \omega_1$.

We now imagine these three stat. liquids, which we shall call $L(s_1)$, $L(s_2)$ and $L(s_3)$, represented in fig. 5 by the points s_1 , s_2 and s_3 ; in each of these points, therefore:

$$\omega_2 A_2 - \omega_1 A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

is zero. It is now easy to find that (22) is positive from i_1 to s_1 (fig. 5) negative from s_1 to s_2 , positive again from s_2 to s_3 and at last negative

again from s_3 to i_2 [comp. the signs in fig. 5]. It now follows from (13) that the variable liquid will move according to the arrows in fig. 5.



If at the beginning of the osmosis the var. liq. L of system (1) is given such a composition, that it is represented at the beginning of the osmosis by a point somewhere to the left of s_2 (fig. 5), then it will move during the osmosis towards s_1 , where it passes into the stationary liquid $L(s_1)$.

When, however, the var. liq. is represented at the beginning of the osmosis by a point to the right of s_2 , it will move towards point s_3 , where it passes into the stat. liq. $L(s_3)$.

From this it also appears that the var. liq. cannot move towards point s_2 . So in system (3) we can get the stat. liq. $L(s_2)$ only then when we bring it already into system (1) at the beginning of the osmosis. This condition is unstable then however, for any small disturbance will cause this liquid $L(s_2)$ to move towards s_1 or s_3 ; consequently we may leave point s_2 and the stat. liq. $L(s_2)$ out of consideration. From this it follows:

when $\omega_2 : \omega_1$ is situated between definite limits, then it is possible that two quite different stat. liquids will be formed at the transition of system (1) into the stat. system (3); it depends upon the composition we give to the var. liq. at the beginning of the osmosis, which of these two liquids will then occur.

It is now quite easy for the reader to deduce himself that the points s_1 and s_2 or s_2 and s_3 of fig. 5 coincide at a certain value of $\omega_2 : \omega_1$ (viz. p or q), so that fig. 5 passes into fig. 2.

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(To be continued.)