

Chemistry. — “Equilibria in systems in which phases, separated by a semipermeable membrane.” VII. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 28, 1925).

Osmotic equilibria and -complexes; the membrane-phase-rule.

We take an osmotic system:

$$E = \left[E_1(n_1 r_1) \mid E_2(n_2 r_2) \right] \dots \dots \dots (1)$$

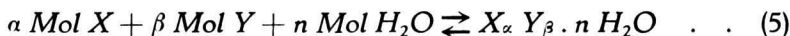
in which E_1 consists of n_1 components in r_1 phases and E_2 of n_2 components in r_2 phases. Let us take as examples the systems:

$$\left(L \mid L_1 \right) ; \left(X + L \mid L_1 \right) ; \left(X + Y + L \mid L_1 \right) \dots (2)$$

$$\left(X + X \cdot n H_2O \mid L \right) \dots \dots \dots (3)$$

$$\left(X + Y + X_\alpha Y_\beta \cdot n H_2O \mid L \right) \dots \dots \dots (4)$$

in which L and L_1 represent aqueous liquids. If water is the diffusing substance, then a little water may diffuse from right to left and reversally, without a new phase is formed or an existing phase disappears totally. This is always the case when a liquid occurs on both sides of the membrane, as in the systems (2). In the systems (3) and (4) a reaction takes place on the left side on taking in or losing water; this reaction is for system (4):



Let us take now the systems:

$$\left(X \mid L \right) ; \left(X \cdot n H_2O \mid L \right) \dots \dots \dots (6)$$

$$\left(X + Y \mid L \right) \dots \dots \dots (7)$$

$$\left(X + X_\alpha Y_\beta \cdot n H_2O \mid L \right) \dots \dots \dots (8)$$

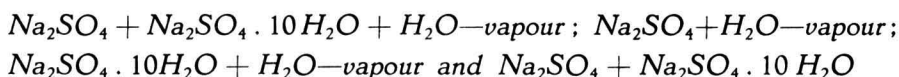
In system (7) and in the first one of the systems (6) no water can diffuse from left to right; if water diffuses from right to left, then on the left side a new phase must arise, f.i. a liquid, a hydrate or water-vapour.

In system (8) and the second one of the systems (6) water is present as well at the right as at the left side of the membrane; with diffusion

of water, independent in which direction, a new phase must be formed at the left side.

Consequently, diffusion of a little water causes in the systems (6)—(8) always the occurrence of one or more new phases, so that the system totally changes its character; in the systems (2)—(4), however, only a small change occurs either in the quantities or in the compositions of the phases, which exist already.

For this reason we shall say that the systems (2)—(4) are osmotic equilibria and the systems (6)—(8) complexes. This may be compared f. i. with the systems:



the first one of which is an equilibrium, but the other three are only complexes, in which nothing may take place without a new phase is formed.

We now take the case that there are two diffusing substances f. i. water and the substance Y . Then the systems (2) and (4) are in osmotic equilibrium with respect to both the diffusing substances. Small quantities of water and Y viz. may diffuse, independent from one another, in both directions, without a new phase is occurring. System (3), however, is only in osmotic equilibrium with respect to water, but not with respect to Y .

The systems (6) are, neither with respect to water, nor with respect to Y , osmotic equilibria, but complexes; system (7) is a complex with respect to water, but an osmotic equilibrium with respect to Y .

System (8) shows something particular; this is viz. a complex, as well with respect to water only as with respect to Y only. If, however, both substances diffuse in a definite ratio viz. n Mol. H_2O : β Mol. Y , then reaction (5) may occur and the complex behaves like an osmotic equilibrium; we will call it preliminarily osmotic.

Consequently we find: with respect to both the diffusing substances the osmotic system can be:

- either a complex (system 6)
- or an osmotic equilibrium (systems 2 and 4)
- or a preliminarily osmotic equilibrium (system 8)
- or a complex with respect to the one diffusing substance and an osmotic equilibrium with respect to the other diffusing substance (systems 3 and 7).

If three or more diffusing substances occur, then similar cases may be distinguished.

The membrane-phase-rule.

We take the osmotic equilibrium:

$$E = E_1(n_1 r_1) | E_2(n_2 r_2) \dots \dots \dots (9)$$

in which E_1 consists of n_1 components in r_1 phases under a pressure P_1 and E_2 of n_2 components in r_2 phases under a pressure P_2 . The phase-rule of GIBBS is valid for each of the two systems separately; therefore, at constant temperature E_1 has $n_1 - r_1 + 1$ freedoms and E_2 has $n_2 - r_2 + 1$ freedoms; consequently the total system has $n_1 + n_2 - (r_1 + r_2) + 2$ freedoms.

When E_1 and E_2 are in osmotic equilibrium with one another with respect to the diffusing substance W , then, as we have seen in the previous communication, there is an equation, which expresses that the O.W.A. of E_1 is equal to that of E_2 . The total number of freedoms is diminished, therefore, with one.

When E_1 and E_2 are in osmotic equilibrium with respect to d diffusing substances, then there are d equations; the total number of freedoms is diminished, therefore, with d .

Consequently we may say:

the number of freedoms of an osmotic equilibrium:

$$E_1(n_1 r_1) | E_2(n_2 r_2)$$

in which d diffusing substances occur, is at constant temperature:

$$n_1 + n_2 - (r_1 + r_2) + 2 - d \dots \dots \dots (10a)$$

consequently equal to the sum of the freedoms of both systems separately, diminished with the number of diffusing substances.

If we take also the temperature variable, then the number of freedoms becomes:

$$n_1 + n_2 - (r_1 + r_2) + 3 - d \dots \dots \dots (10b)$$

We shall apply this to some of the systems, formerly discussed. Let us take f.i. the osmotic equilibrium:

$$E = \left(\text{water} | L \right) \dots \dots \dots (11)$$

in which water is the diffusing substance and L a binary liquid. At constant temperature the left system has one freedom and the right one has two freedoms. As there is one diffusing substance, the total system has $1 + 2 - 1 = 2$ freedoms, therefore.

We now give to the water a definite pressure P_0 , so that one freedom disappears; consequently the total system has still one freedom. Therefore to each concentration of the liquid L belongs a definite pressure P and consequently also a definite osmotic pressure $P - P_0$ of this liquid.

Let us take the osmotic equilibrium:

$$E = L_1 | L_2 \dots \dots \dots (12)$$

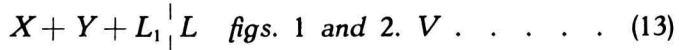
with one diffusing substance f.i. water; we assume that both liquids are

ternary. If we keep temperature and pressure constant (the pressure may be for both liquids equal or different) then each liquid has 2 freedoms; the total system has, therefore, $2 + 2 - 1 = 3$ freedoms.

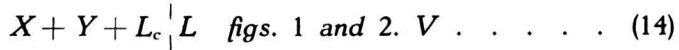
If we take for L_1 a liquid of definite composition, then 2 freedoms disappear; consequently L_2 has still one freedom; it is represented, therefore, in a diagram by a curve. If both liquids have the same pressure and if they consist of the same components, then this is the isotonic curve, formerly discussed, which goes through the point, representing liquid L_1 .

We now take some equilibria, which are represented in the figures of the communications III—V. In order to remain in accordance with those diagrams, we assume that there is one diffusing substance viz. $W =$ water and that the pressure of both the separate systems is equal and constant.

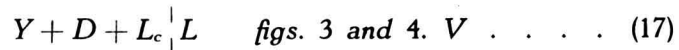
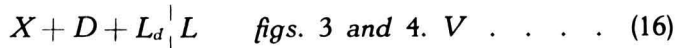
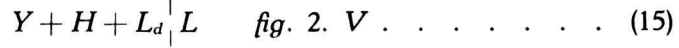
In the osmotic equilibrium:



the left system has no more a freedom, as T and P are constant; liquid L_1 must have, therefore, a definite composition viz. c ; we represent it by L_c . (13) becomes, therefore:

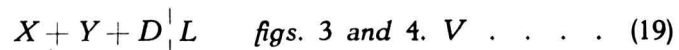
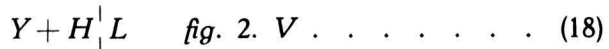


Also in the osmotic equilibria:



the liquids on the left side of the membrane must have the indicated composition. As the systems (14)—(17) are osmotic equilibria with one diffusing substance, as the left system is zero and the right one has two freedoms, the total number becomes, therefore, $0 + 2 - 1 = 1$ freedom. Consequently the liquid L is monovariant ($P.T$) and is represented, therefore, by a curve. In system (14) this is the isotonic curve, not-drawn, going through point c , all points of which, except point c itself, represent metastable liquids; in system (15) this is the isotonic curve dn (and its metastable prolongation), etc.

Also the systems:



are osmotic equilibria. As in each of those equilibria the system at the left side of the membrane has no freedom, each of those equilibria has, therefore, $0 + 2 - 1 = 1$ freedom. The liquid L is, therefore, mono-variant ($P.T$) again and is represented by the points of a curve. In (18) this is the same as in (15) viz. curve dn ; in (19) this is, as we have previously seen, a curve, all points of which represent metastable states.

We now take the osmotic equilibrium:

$$Y + L_1 \Big| L \quad \text{figs. 1, 2 and 3. III (20)}$$

in which of course L_1 represents a liquid of wv , viz. of the saturation-curve of Y . As the left system has one freedom and the right one two freedoms, the total equilibrium has, therefore, $1 + 2 - 1 = 2$ freedoms; consequently it is divariant ($P.T$). If we take for L_1 a definite liquid L_a of the saturation-curve, then one freedom disappears; consequently liquid L has still one freedom. It is represented, therefore, by the points of the isotonic curve an . We shall represent those liquids by $L(1-an)$, in which the 1 indicates that the liquids have one freedom and an is, therefore, a curve. Then we may represent the equilibrium by

$$Y + L_a \Big| L(1-an) \quad \text{figs. 1, 2 and 3. III (21)}$$

As we may take for L_1 in (20) each arbitrary liquid of curve wv , we have a.o. also the following equilibria:

$$Y + L_w \Big| L(1-wm) \quad ; \quad Y + L_b \Big| L(1-bo); \text{ etc. (22)}$$

which represent, therefore, just as (21) special cases of (20).

For the osmotic equilibria

$$H + L_1 \Big| L \quad \text{fig. 1. IV (23)}$$

$$D + L_1 \Big| L \quad \text{fig. 2. IV (24)}$$

the same is valid as for (20). Special cases of (23) are a.o.:

$$H + L_w \Big| L(1-wm) \quad ; \quad H + L_c \Big| L(1-ncn'); \text{ etc.}$$

and of (24):

$$D + L_w \Big| L(1-mwm') \quad ; \quad D + L_f \Big| L(1-nfan'); \text{ etc.}$$

The osmotic system:

$$Y \Big| L \quad \text{fig. 1. III (25)}$$

is not an equilibrium, but an osmotic complex; as the diffusing substance does not change, therefore, the number of freedoms, this complex has

$0 + 2 = 2$ freedoms. Consequently liquid L is bivariant ($P.T$) and is represented by the points of a field.

We are able to find the position of this field in the following way. We imagine in (25) the substance Y in equilibrium with a liquid of the saturation-curve wv , f. i. with the liquid a . We then get equilibrium (21). If we take away from this the liquid L_a , then remains the complex:

$$Y \Big| L(1-am) \quad \text{fig. 1. III} \quad (26)$$

The solid substance Y can exist, therefore, in osmotic contact with the liquids of curve am ; consequently this curve must be situated in the field of the liquid L in (25), which is wanted. If we substitute L_a in (21) by L_w or L_b then we get the equilibria (22); the curves wm and bo are situated, therefore, also in the field wanted.

As we may substitute L_a in (21) by any arbitrary liquid of curve wv , all isotonic curves, going through a point of curve wv , are situated, therefore, in the field. Those curves define a field, which we shall represent by $L(2-wmXv)$; the 2 indicates that the liquids have 2 freedoms and that $wmXv$ is a field, therefore. The wanted field of (25) therefore, must either coincide with the field $wmXv$ or extend itself over it. Further we shall see that it coincides with it. Therefore, the osmotic system (25) is defined more closely by:

$$Y \Big| L(2-wmXv) \quad \text{fig. 1. III} \quad (27)$$

Consequently we find, in accordance with our previous considerations: the solid substance Y may be in osmotic contact with the liquids of the field $wmXv$ without taking water from those liquids. Also we may say, therefore:

the $O.W.A.$ of the solid substance Y is smaller than that of the liquids of the field $wmXv$.

In a similar way we find the fields of other osmotic complexes f. i.

$$Y \Big| L(2-ambc) \quad \text{fig. 1. V} \quad (28)$$

$$Y \Big| L(2-dnbc) \quad \text{fig. 2. V} \quad (29)$$

$$H \Big| L(2-wm\circ v) \quad \text{fig. 1. IV} \quad (30)$$

$$H \Big| L(2-amnd) \quad \text{fig. 2. V} \quad (31)$$

$$D \Big| L(2-mwm'p'vp) \quad \text{fig. 2. IV} \quad (32)$$

Hence appears that the liquids which may be in osmotic contact with

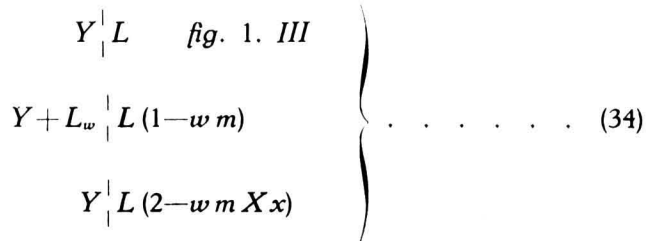
the solid substance, without waterdiffusion, are divariant; they are situated in the indicated field.

We are able to deduce those fields also in the following way. We take the osmotic complex:



We take in the field, sought for, an arbitrary liquid L_x ; as no water diffuses from this towards Y , the O.W.A. of L_x is greater, therefore, than that of the solid substance Y . As L_x changes its place in the field, then it alters its O.W.A., if not, it proceeds along an isotonic curve. We now imagine that L_x changes its place in such a way that its O.W.A. becomes smaller constantly f. i. at a displacement along a straight line in the direction of point W . At a definite composition of L_x its O.W.A. then becomes equal to that of Y and in (33) a little water may diffuse from L_x towards Y . On the left side of the membrane is then formed a little of the liquid L_w ; liquid L_x is represented then by a point of the isotonic curve $w m$.

If L_x is displaced still further towards point W , then its O.W.A. becomes smaller perpetually, then the osmotic complex (33) can exist no more. The field sought for is situated, therefore, at the right of curve $w m$ and is, therefore, the field $w m X Y$ or, if we limit ourselves to the stable part, the field $w m X v$. We shall represent a similar deduction by:



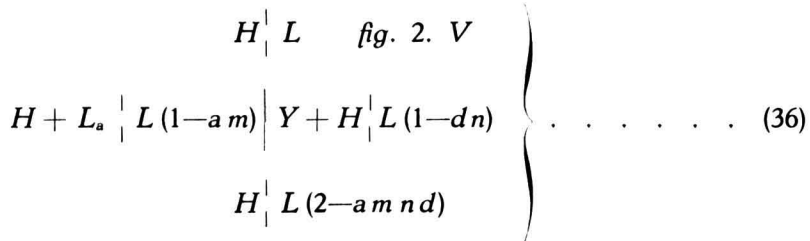
Firstly viz. we write the osmotic complex, the field of which we wish to define, then the osmotic equilibrium which arises with diffusion of a little water and at last the osmotic equilibrium, mentioning the field found.

For the field of the osmotic complex



we find 2 limit-curves. If a liquid proceeds along a straight line towards the point W , then it gives at a definite composition water to H , so that this passes into $H + L_a$; if this liquid proceeds along the straight line in opposite direction, then its O.W.A. increases and it takes water from H

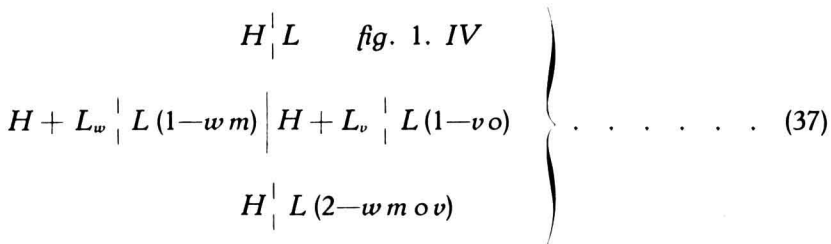
at a definite composition; this then passes into $Y + H$. We now represent this in a similar way as in (34) viz.



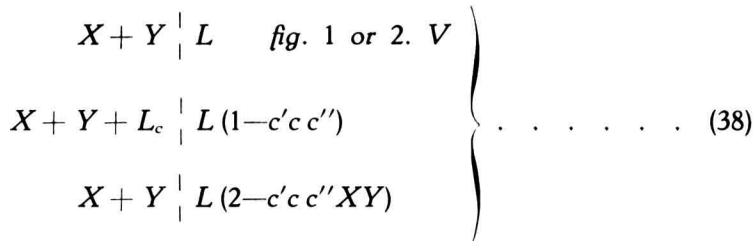
The only difference with (34) is that with diffusion of water, now two different osmotic equilibria may occur; at the left side of the line we write the equilibrium, which arises at diffusion of a little water towards the left, at the right side of the line the equilibrium, which arises at diffusion of a little water towards the right. This result is in accordance with that in (31). We now may say:

the hydrate H can be in osmotic contact with the liquids of the field $amnd$ without it is taking water from those liquids or reversally without it is giving water to them. Liquids, at the left of this field, give water to the hydrate; liquids at the right of this field, take water from the hydrate.

In a similar way we find a.o.:



which is in accordance with (30)

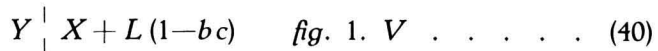


Herein the isotonic curve (not drawn in the figure) going through point c is represented by $c'c''$. The liquids of the field are all supersaturated. As all saturated and unsaturated liquids are situated outside this field, they shall give water to the solid mixture $X + Y$. We may also say, therefore: the O.W.A. of solid $X + Y$ is greater than that of all saturated and unsaturated liquids.

We now take the osmotic complex:



in which a solid substance is on both sides of the membrane. As the liquid is saturated with solid X , L in (39) can be represented only by points of curve bc . As the *O.W.A.* of the solid substance Y is equal to that of the liquids of curve am , the *O.W.A.* of the solid substance Y is also smaller, therefore, than that of all liquids of curve bc . Consequently we may write for (39):

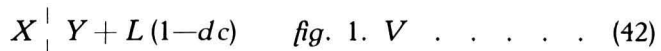


Therefore, the solid substance Y may be in osmotic contact with all liquids, which are saturated with solid X , without taking water from those liquids.

Otherwise it is, however, in the osmotic complex:



in which the liquids, saturated with Y are represented by points of curve ac . The *O.W.A.* of the substance X is equal to that of the liquids of curve bd ; consequently point d divides curve ac into two parts; as the liquids of part dc have a greater *O.W.A.* than that of liquid d and, therefore, also a greater *O.W.A.* than the solid substance X , we may write for (41):



Consequently the solid substance X cannot be in osmotic contact with all liquids, saturated with solid Y , but only with the liquids, which are represented by part dc of the saturation-curve; if we bring in osmotic contact solid X with liquids of part ad of this saturation-curve, then X shall flow away totally or partially.

(To be continued).

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