

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

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The membrane-phase-rule and the membrane.

In the previous communication we have seen that an osmotic equilibrium:

$$E = E_1 (n_1 r_1) \mid E_2 (n_2 r_2) \dots \dots \dots (1)$$

in which are present d substances, which diffuse by the membrane, has

$$(n_1 + n_2) - (r_1 + r_2) + 3 - d \dots \dots \dots (2)$$

freedoms. If we assume that both the separate systems E_1 and E_2 have the same pressure, then, therefore, equilibrium (1) has:

$$(n_1 + n_2) - (r_1 + r_2) + 2 - d \dots \dots \dots (3)$$

freedoms. We are able to deduce this and other properties also in the following way. Let us take f.i. the osmotic equilibrium:

$$E = L_1 \mid L_2 \dots \dots \dots (4)$$

in which L_1 and L_2 represent two liquids;

$$L_1 \text{ contains the components } A_1 B_1 \dots XY \dots UV \text{ and } W \dots (5)$$

$$L_2 \text{ „ „ „ } A_2 B_2 \dots XY \dots UV \text{ and } W \dots (6)$$

Consequently both liquids contain the common components $XY \dots UV$ and W ; we assume that the d components UV and W are able to diffuse by the membrane, in contrary with the others viz. $XY \dots$

Those components $XY \dots$ behave, therefore, in both the liquids as if they are different substances; we may imagine them to be replaced in L_1 by the components $X_1 Y_1 \dots$ and in L_2 by $X_2 Y_2 \dots$; we then have two new liquids L'_1 and L'_2 in which

$$L'_1 \text{ contains the components } A_1 B_1 \dots X_1 Y_1 \dots UV \text{ and } W \dots (7)$$

and

$$L'_2 \text{ „ „ „ } A_2 B_2 \dots X_2 Y_2 \dots UV \text{ and } W \dots (8)$$

We now may imagine the osmotic equilibrium (4) to be substituted by the equilibrium:

$$E' = L'_1 + L'_2 \dots \dots \dots (9)$$

if we assume that only the components UV and W dissolve in both the liquid-phases. When in liquid L_1 [viz. in (5)] the number of components is n_1 and in liquid L_2 [viz. in (6)] the number is n_2 , then follows from (7) and (8) that equilibrium (9) consists of $n_1 + n_2 - d$ components. Consequently, in accordance with the phase-rule of GIBBS, equilibrium (9) has:

$$(n_1 + n_2 - d) - 2 + 2 = n_1 + n_2 - d \text{ freedoms . . . (10)}$$

so that the osmotic equilibrium (4) has the same number of freedoms. This is also in accordance with the membrane-phase-rule; if we put viz. in (3) the number of phases $r_1 + r_2 = 2$, then (3) passes into (10).

We now make the same supposition for the components of system (1) as above for those of system (4); we then may imagine the osmotic equilibrium (1) to be replaced by the equilibrium:

$$E' = E'_1 + E'_2 \text{ (11)}$$

which consists of $n_1 + n_2 - d$ components. As there are $r_1 + r_2$ phases, (11) and consequently also the osmotic equilibrium (1) has

$$(n_1 + n_2 - d) - (r_1 + r_2) + 2$$

freedoms; therefore, we re-find (3).

Till now with our considerations we have made no supposition on the character of the membrane and on its action; we shall call a similar membrane, the character and action of which is not defined more closely, a "theoretical" membrane.

However, we may assume also that the membrane consists of a phase M , which, under definite conditions, permits some substance to diffuse, and other ones not; we shall represent this membrane, consisting of one phase M , by $|M|$ and call it a "real" membrane.

We now replace the theoretical membrane in (1) by a real membrane, so that we get the equilibrium

$$E = E_1(n_1 r_1) + |M| + E_2(n_2 r_2) \text{ (12)}$$

We adjoin the following properties to this real membrane, consequently to the phase M :

1. It separates the two systems in such a way that the phases of E_1 do not come in direct contact with those of E_2 ;
2. It contains one or more substances MN etc., which do not occur in the systems E_1 and E_2 and which do not dissolve in those systems;
3. From the substances, which occur in the systems E_1 and E_2 , some are taken in by the membrane but others not; it forms with the taken substances a phase of variable composition.

We may imagine this real membrane f. i. as a solid solution or also as a thick, tuff, strongy viscous or jellied liquid or in another way. It

stands to reason that it depends on the character of the membrane and on its strange substances MN etc. which substances will be taken in or not from the systems E_1 and E_2 .

If we imagine for this real membrane a liquid, then theoretically this will probably be able to take in all substances from E_1 and E_2 ; practically, however, this need not be the case, the same f.i. a vapour does not contain practically all substances, which are present in the system, in which it participates.

We now are able to show: the real membrane $|M|$ which takes d substances from the systems E_1 and E_2 , behaves like a theoretical membrane, by which these d substances may diffuse.

In order to show the above-mentioned, we firstly shall deduce the equations for equilibrium, which are valid for the osmotic equilibrium (1); for the sake of simplicity we assume that there is one diffusing substance only, viz. W .

We consider a system

$$E_A = A_1 + A_2 \dots + A_r \dots \dots \dots (13)$$

in which we give to an arbitrary phase A_i the composition:

$$A_i = x_i X + y_i Y + \dots + w_i W \dots \dots \dots (14)$$

$$i = 1, 2, \dots r$$

We call ζ_i the thermodynamical potential of this phase A_i When this system E_A is in equilibrium, then must be:

$$0 = \left. \begin{aligned} & \frac{\partial \zeta_1}{\partial X} dx_1 + \frac{\partial \zeta_2}{\partial X} dx_2 \dots + \frac{\partial \zeta_1}{\partial Y} dy_1 + \frac{\partial \zeta_2}{\partial Y} dy_2 \dots \\ & \dots + \frac{\partial \zeta_1}{\partial W} dw_1 + \frac{\partial \zeta_2}{\partial W} dw_2 \dots + \frac{\partial \zeta_r}{\partial W} dw_r \end{aligned} \right\} \dots \dots (15)$$

while the conditions:

$$\left. \begin{aligned} 0 &= dx_1 + dx_2 \dots + dx_r \\ 0 &= dy_1 + dy_2 \dots + dy_r \\ & \dots \dots \dots \end{aligned} \right\} \dots \dots \dots (16)$$

$$0 = dw_1 + dw_2 \dots + dw_r \dots \dots \dots (17)$$

must be satisfied.

From this we find in the known way the equations for equilibrium:

$$\frac{\partial \zeta_1}{\partial X} = \frac{\partial \zeta_2}{\partial X} = \dots = \frac{\partial \zeta_r}{\partial X} \quad \frac{\partial \zeta_1}{\partial Y} = \frac{\partial \zeta_2}{\partial Y} = \dots = \frac{\partial \zeta_r}{\partial Y} \text{ etc. } \dots \dots (18)$$

$$\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \frac{\partial \zeta_3}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \dots \dots \dots (19)$$

If A_1 is a phase of constant composition, viz. dx_1 and dy_1 satisfy the relations:

$$\frac{dx_1}{x_1} = \frac{dy_1}{y_1} = \dots = \frac{dw_1}{w_1} \dots \dots \dots (20)$$

then in (18) and (19) the terms with the index 1 disappear and we get a new equation:

$$\zeta_1 - x_1 \frac{\partial \zeta_k}{\partial X} - y_1 \frac{\partial \zeta_k}{\partial Y} \dots - w_1 \frac{\partial \zeta_k}{\partial W} \dots \dots \dots (21)$$

in which k represents one of the indices 2, 3, . . . , r .

For a system:

$$E_B = B_1 + B_2 + \dots \dots \dots (22)$$

of course similar equations are valid as for E_A , consequently equations, which correspond with (15) – (21); for this reason we shall call the equations, valid for E_A the equations (15 A) – (21 A), and those, valid for B , the equations (15 B) – (21 B).

We now are able to deduce the equations for equilibrium, which are valid for the osmotic equilibrium:

$$E = E_A \mid E_B \dots \dots \dots (23)$$

in the following way. As now no more the thermodynamical potential of each of the separate systems E_A and E_B must be zero, but that of the complete system E , the equations (15 A) and (15 B) are no more valid each for itself, but we get:

$$0 = (15 A) + (15 B) \dots \dots \dots (24)$$

the meaning of which is clear.

The changes $dx_1 dx_2$ etc. which refer to the not-diffusing substances, satisfy the equations (16 A) and (16 B). As, however, the quantity of the diffusing substance W must not rest constant now in each of the separate systems E_A and E_B but it must in the complete equilibrium E the equations (17A) and (17B) disappear, therefore; they are substituted by the one equation:

$$0 = (dw_1 + dw_2 + \dots)_A + (dw_1 + dw_2 + \dots)_B = 0 \dots (25)$$

Consequently for the osmotic equilibrium are valid the equations: (24), (25), (16 A) and (16 B).

If we deduce from this in the well-known way the equations for equilibrium, then we find:

$$\text{the equations (18 A) and (18 B)}$$

and still the equations:

$$\left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots \right)_A = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots \right)_B \dots \dots (26)$$

Those equations (26) involve not only the equations (19 A) and (19 B) but also still one new equation, viz.:

$$\left(\frac{\partial \zeta_k}{\partial W}\right)_A = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \dots \dots \dots (27)$$

in which, as follows from (26), we may take the indices k and l arbitrarily. Consequently we find for the osmotic equilibrium (23):

1° the equations for equilibrium, which are valid for each of the systems E_A and E_B separately;

2° besides a new equation for equilibrium viz. (27); this expresses that the osmotic water-attraction of both the systems E_A and E_B is equal.

We now consider the osmotic equilibrium:

$$E = E_A + |M| + E_B \dots \dots \dots (28)$$

and we assume that the real membrane $|M|$ has the composition:

$$mM + nN + oO + \dots + wW \dots \dots \dots (29)$$

and the thermodynamical potential ζ . Instead of (24) we now get:

$$o = (15 A) + \frac{\partial \zeta}{\partial W} \cdot dw + (15 B) \dots \dots \dots (30)$$

This equation expresses that the thermodynamical potential of the complete system (28) must be a minimum. The variables dm, dn etc. of the strange substances $M N$ etc. of the membrane do not occur in this equation.

The equations (16 A) and (16 B), which refer to the not-diffusing substances of the systems E_A and E_B rest unchanged; equation (25), however, passes into:

$$o = (dw_1 + dw_2 + \dots)_A + dw + (dw_1 + dw_2 + \dots)_B \dots \dots (31)$$

this expresses that the quantity of the diffusing substance W , which is present in the complete system (28), remains constant. Consequently for system (28) we have the equations: (30), (31), (16 A) and (16 B).

If we deduce from this in the known way the equations for equilibrium, then we find, besides the equations (18 A) and (18 B) still also:

$$\left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots\right)_A = \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots\right)_B \dots \dots (32)$$

Those equations (32) involve not only the equations (26) but yet also a new equation, viz.

$$\frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_k}{\partial W}\right)_A \text{ or } \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \dots \dots \dots (33)$$

in which we may take arbitrarily the indices k and l . Consequently we find for the equilibrium (28)

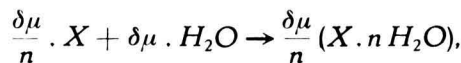
1° the same equations for equilibrium which are valid for the osmotic equilibrium (23)

2° besides a new equation (33); this expresses that the O.W.A. of the real membrane is equal to that of each of both the systems E_A and E_B separately. This equation defines also the concentration of the substance W in the membrane.

It appears from this, therefore, that the state of the separate systems E_A and E_B is defined by the same equations, immaterial whether those systems, as in (23) are in osmotic contact with the aid of a theoretical membrane, or, as in (28) with the aid of a real membrane.

Yet there may be any difference in the finishing-equilibrium of (23) and (28) if we start from definite systems (23) and (28). In the state of equilibrium of (28) viz. the real membrane must have a definite concentration of the substance W ; had this concentration beforehand been different, then the membrane must take in a little water from the systems E_A and E_B or it has to give water to them. This quantity, and consequently also the influence on the final equilibrium, can be the greater, the greater is the mass of the real membrane. If the mass of the membrane is small with respect to that of E_A and E_B , then this influence may be neglected practically.

In the previous considerations we have supposed that each of the systems E_A and E_B contains one liquid at least. This is valid, however, also, if one of the systems consists of substances of constant composition, between which a phases-reaction may occur by taking in or giving water. If one of those systems consists f. i. of a solid substance X and its hydrate $X \cdot nH_2O$, then on admittance of $\delta\mu$ quantities of water occurs the reaction:



consequently a reaction, with which the quantities of the phases change, but their compositions remain constant.

We now assume that in the system E_A on increase or loss of water a similar phases-reaction may occur. The increase of the thermodynamical potential on increase of $\delta\mu$ quantities of water, is represented by $\frac{\partial Z_A}{\partial W} \cdot \delta\mu$ so that $\frac{\partial Z_A}{\partial W}$ defines the O.W.A. of system E_A .

For equilibrium (23) is valid now, instead of (24):

$$o = \frac{\partial Z_A}{\partial W} \cdot \delta\mu + (15 B) \quad (34)$$

the equations (16 A) disappear, but (16 B) remain valid. Instead of (25) we now get, however;

$$o = \delta\mu + (dw_1 + dw_2 + \dots)_B \quad (35)$$

If we deduce again from this the equations for equilibrium, then we find firstly the equations (18 B) and moreover:

$$\frac{\partial Z_A}{\partial W} = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \right)_B \dots \dots \dots (36)$$

This contains not only the equations (19B) but still one equation more; this expresses that the O. W. A. of system E_A is equal to that of system E_B .

We now take, instead of equilibrium (23) with the theoretical membrane, equilibrium (28) with the real membrane. Then we have to replace (34) and (35) by:

$$\begin{aligned} 0 &= \frac{\partial Z_A}{\partial W} \cdot d\mu + \frac{\partial \zeta}{\partial W} \cdot dw + (15 B) \\ 0 &= d\mu + dw + (dw_1 + dw_2 \dots)_B. \end{aligned}$$

We find from this again the same conditions for equilibrium (18 B) and also:

$$\frac{\partial Z_A}{\partial W} = \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \right)_B.$$

Those last equations contain not only the equations (36) but moreover one, which expresses that the O. W. A. of the real membrane is equal to that of the systems E_A and E_B .

Consequently it appears from this that the deduced above on the correspondance of a system with a theoretical and a real membrane, is also true, if one of the separate systems consists of substances of constant composition, between which on increase or loss of water a phasesreaction occurs.

We may extend those considerations also to an osmotic equilibrium:

$$E = E_A + |E_0| + E_B$$

in which $|E_0|$ represents a real membrane, which consists of different phases and which has similar properties, as are discussed above for $|M|$. In similar way as above we find for this:

1^o. the equations for equilibrium, which are valid for each of the three systems E_A E_0 and E_B separately;

2^o. two equations, which express that the O.W.A. of the three systems is the same.

(To be continued.)

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