Chemistry. — *Change of the Osmotic Water Attraction of a system of phases.* I. By F. A. H. SCHREINEMAKERS.

In discussing the osmosis we have until now confined ourselves in most cases to systems, in which there was a liquid on both sides of the membrane. Now we shall consider the general osmotic system:

$$E \mid E' \qquad \qquad \text{(1)}$$

in which E (and E') can represent not only a single phase (e.g. a liquid or a vapour) but also a system of two or more phases;

e.g. a liquid + a vapour

or: a liquid + one or more solid substances, etc. As we assume that the phases of E (and E') are in equilibrium with one another, we shall call E (and E') an equilibrium.

We now take the osmotic system:

$$E(P) \mid E'(P') \qquad \longleftarrow \delta a \qquad \text{(2)}$$

in which the pressure is P on the left side of the membrane and P' on the right side. We now represent the Th. d. pot. (thermodynamical potential) of $E(P)$, viz. of the equilibrium E under the pressure P by Z and that of $E'(P')$ by Z'; the total Th. d. pot. of system (2) then will be $Z + Z'$.

We now imagine that δa mol. water diffuse from E' towards E, so that the condition on the two sides of the membrane changes a little; then the Th. d. pot. will increase on the left side with:

$$\frac{dZ}{da} \cdot \delta a + \frac{1}{2} \frac{d^2Z}{da^2} \cdot \delta a^2 + \ldots \qquad \text{(3)}$$

and on the right side of the membrane with:

$$-\frac{dZ'}{da} \cdot \delta a + \frac{1}{2} \frac{d^2Z}{da^2} \cdot \delta a^2 - \ldots \qquad \text{(4)}$$

it is clear that (3) obtains for the pressure P and (4) for the pressure P'. So the Th. d. pot. of the entire system increases with:

$$\left(\frac{dZ}{da} - \frac{dZ'}{da} \right) \delta a + \frac{1}{2} \left(\frac{d^2Z}{da^2} + \frac{d^2Z'}{da^2} \right) \delta a^2 + \qquad \text{(5)}$$

As this total Th. d. pot. may decrease or remain constant only, δa must, therefore, satisfy:

$$\left(\frac{dZ'}{da} - \frac{dZ}{da} \right) \delta a - \frac{1}{2} A \cdot \delta a^2 \ldots \geqq 0 \qquad \text{(6)}$$

in which, as we shall see further on, A is positive.

In deducing all this we have assumed that with the diffusion of δa mol. water the W-amount of the membrane does not change; with real membranes, however, it does change. When, however, the membrane is small with respect to the quantities of both equilibria, this change will generally play only a part of minor importance; we shall refer to this later on.

In (2) we have assumed that the pressure remains constant on the two sides of the membrane. In the osmotic system:

$$E\,(V)\mid E'\,(V') \qquad \longleftarrow \delta a \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the equilibrium E, however, has been shut into a space with a constant volume V and the equilibrium E' in a space with a constant volume V'. Then the pressure in these spaces may change continually during the osmosis. If we represent the free energy of E and E' (in the volumina V and V') by ψ and ψ', then the total free energy will, therefore, be $\psi + \psi'$. When δa mol. water now diffuse from E' towards E, then we find that δa must satisfy:

$$\left(\frac{d\psi'}{da} - \frac{d\psi}{da}\right)\delta a - \frac{1}{2}\,B\,\delta a^2 \ldots \geqq 0 \quad . \quad . \quad . \quad . \quad (8)$$

in which B is positive, as we shall see further on.

We can prove now that

$$\left(\frac{dZ}{da}\right)_P = \left(\frac{d\psi}{da}\right)_V . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

When the equilibrium E namely takes in δa mol. water and changes its pressure with δP, then we have:

$$dZ = \left(\frac{dZ}{da}\right)_P \delta a + \left(\frac{dZ}{dP}\right)_a dP = \left(\frac{dZ}{da}\right)_P \delta a + V\,dP \quad . \quad . \quad (10)$$

We now choose δa and δP in such a way that the total volume V remains unchanged; (10) then passes into:

$$\left(\frac{dZ}{da}\right)_V = \left(\frac{dZ}{da}\right)_P + V\left(\frac{dP}{da}\right)_V . \quad . \quad . \quad . \quad . \quad (11)$$

We now have:

$$\left(\frac{dZ}{da}\right)_V = \left[\frac{d\,(\psi + PV)}{da}\right]_V = \left(\frac{d\psi}{da}\right)_V + V\left(\frac{dP}{da}\right)_V . \quad . \quad . \quad (12)$$

(9) now follows from (11) and (12). We now put:

$$\xi = -\left(\frac{dZ}{da}\right)_P = -\left(\frac{d\psi}{da}\right)_V \quad \text{and} \quad \xi' = -\left(\frac{dZ'}{da}\right)_{P'} = -\left(\frac{d\psi'}{da}\right)_{V'} \quad (13)$$

Then it follows from (6) and (8) that δa in system (2) must satisfy:

$$(\xi - \xi') \, \delta a - \frac{1}{2} A \cdot \delta a^2 \ldots \geqq 0 \ . \quad . \quad . \quad . \quad . \quad (14)$$

and in system (7):

$$(\xi - \xi') \, \delta a - \frac{1}{2} B \cdot \delta a^2 \ldots \geqq 0 \ . \quad . \quad . \quad . \quad . \quad (15)$$

We now distinguish three cases.

1. $\xi > \xi'$. As δa^2 is small with respect to δa, the signs of (14) and (15) will be determined by the first term; so δa must satisfy:

$$(\xi - \xi') \, \delta a > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

As the coefficient of δa is positive, δa must consequently be positive also; so in (2) and (7) the water will diffuse in the direction of the arrow, viz. towards the left.

2. $\xi < \xi'$. We now see that δa must be negative; the water will now diffuse in (2) and (7) in a direction opposite to that of the arrow, viz. towards the right.

3. $\xi = \xi'$. Instead of (14) and (15) we now have:

$$-\frac{1}{2} A \cdot \delta a^2 \geqq 0 \quad \text{and} \quad -\frac{1}{2} B \cdot \delta a^2 \geqq 0 . \quad . \quad . \quad (17)$$

As A and B are positive and δa^2 is also positive for all values of δa, we can therefore only satisfy (17) by $\delta a = 0$. Then no water passes through the membrane, so that the two equilibria are in osmotic equilibrium.

We see from this that it depends on the values of ξ and ξ' (namely on their difference) whether water will diffuse and in what direction this will take place. We now call ξ the O. W. A. of the equilibrium E (under the pressure P or in the volume V) and ξ' the O. W. A. of the equilibrium E' (under the pressure P' or in the volume V'). We now may say, as it appears from 1, 2 and 3:

I. When the pressures or the volumina remain constant on both sides of a membrane $M(W)$,

then the water diffuses towards that side of the membrane, where the O. W. A. is greatest,

and no water diffuses when the O. W. A. is equal on both sides.

In preceding communications we have deduced corresponding rules for the case in which there is only one liquid on the two sides of the membrane.

The rules deduced above also obtain for an osmotic system:

$$E\,(P) \mid E'\,(V') \qquad \longleftarrow \delta a \quad . \quad . \quad . \quad . \quad (18)$$

in which the pressure remains constant on the one side of the membrane and the volume on the other side.

Before discussing the osmosis in similar systems, we shall first discuss the influence of different factors on the O. W. A. of an equilibrium.

Influence of pressure or volume on the O.W.A. of an equilibrium.

As we have seen above, the O. W. A. of an arbitrary equilibrium E (and consequently also that of a liquid or vapour) is determined by:

$$\xi = -\left(\frac{dZ}{da}\right)_P \quad \text{or} \quad \xi = -\left(\frac{d\psi}{da}\right)_V \quad . \quad . \quad . \quad . \quad (19)$$

From this follows:

$$d\xi = -\left(\frac{dV}{da}\right)_P \cdot dP \quad \text{and} \quad d\xi = +\left(\frac{dP}{da}\right)_V \cdot dV \quad . \quad . \quad . \quad (20)$$

From this follows:

II^a. When we increase the pressure of an equilibrium (dP pos.), then its O.W. A. will decrease, when the volume increases with the absorption of water (the pressure remaining constant).

II^b. When we diminish the volume of an equilibrium (dV neg.) then its O.W. A. will decrease, when the pressure increases (the volume remaining constant).

Between these two changes of the O.W. A. the relation:

$$\frac{d\xi}{dV} = \left(\frac{dP}{dV}\right)_\alpha \cdot \frac{d\xi}{dP} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

exists.

Later on we shall refer to this relation and the preceding ones.

Influence of the absorption (emission) of water on the O. W. A. of an equilibrium.

When an equilibrium is in a stable condition, the Th. d. pot. must remain constant or increase a little with every small internal change, taking place at constant T and P. We now suppose all phases of this equilibrium divided by a membrane into two equal parts, which we shall call E; then we have the osmotic system:

$$E(P) \mid E(P) \quad \longleftarrow \delta a \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$
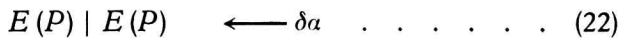
in which the pressure is equal on both sides. When δa mol. water now diffuse towards the left, the Th. d. pot. will increase on the left side with:

$$\frac{dZ}{da} \delta a + \frac{1}{2}\left(\frac{d^2Z}{da^2}\right)\delta a^2 + \ldots \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and on the right side of the membrane with:

$$-\frac{dZ}{da}\delta a + \frac{1}{2}\left(\frac{d^2Z}{da^2}\right)\delta a^2 - \ldots \quad . \quad . \quad . \quad . \quad (24)$$

As the total Th. d. pot. now increases with

$$\frac{d^2Z}{da^2} \cdot \delta a^2 + \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

it follows that the coefficient of δa^2 must be positive or (in special cases) zero. As:

$$\xi = -\left(\frac{dZ}{da}\right)_P \text{ and } \left(\frac{d\xi}{da}\right) = -\left(\frac{d^2Z}{da^2}\right)_P \quad \ldots \quad (26)$$

follows:

$$\left(\frac{d\xi}{da}\right)_P \leqq 0 \quad \ldots \quad \ldots \quad \ldots \quad (27)$$

If instead of (22) we take the osmotic system

$$E(V) \mid E(V) \quad \longleftarrow \delta a \quad \ldots \quad \ldots \quad (28)$$

in which the volume is equal on both sides of the membrane, then we find:

$$\left(\frac{d\xi}{da}\right)_V \leqq 0 \quad \ldots \quad \ldots \quad \ldots \quad (29)$$

If we take an equilibrium the pressure of which remains constant, "P const." and an equilibrium, the volume of which remains constant, "V const." then we may say:

III^a. when an equilibrium (P const.) takes in water, its O. W. A. will decrease; only in the special case that all phases keep the same composition, the O. W. A. will remain unchanged.

III^b. when an equilibrium (V const.) takes in water, its O. W. A. will decrease; only in special cases the O. W. A. will remain unchanged.

Between the changes of the O. W. A. mentioned in III^a. and III^b. the relation

$$\left(\frac{d\xi}{da}\right)_V = \left(\frac{d\xi}{da}\right)_P + \left(\frac{dP}{dV}\right)_a \cdot \left(\frac{dV}{da}\right)_P^2 \quad \ldots \quad (30)$$

exists. In order to deduce it we suppose that an equilibrium takes in δa mol. water, the pressure changing with dP at the same time; we then have:

$$d\xi = \left(\frac{d\xi}{da}\right)_P da + \left(\frac{d\xi}{dP}\right)_a dP \quad \ldots \quad \ldots \quad (31)$$

We now imagine δa and δP chosen in such a way that the total volume remains constant; then (31) passes into:

$$\left(\frac{d\xi}{da}\right)_V = \left(\frac{d\xi}{da}\right)_P + \left(\frac{d\xi}{dP}\right)_a \cdot \left(\frac{dP}{da}\right)_V \quad \ldots \quad (32)$$

which with the aid of (20) passes into:

$$\left(\frac{d\xi}{da}\right)_V = \left(\frac{d\xi}{da}\right)_P - \left(\frac{dV}{da}\right)_P \cdot \left(\frac{dP}{da}\right)_V \quad \ldots \quad (33)$$

We also have:

$$dP = \left(\frac{dP}{da}\right)_V \cdot da + \left(\frac{dP}{dV}\right)_\alpha dV \quad . \quad . \quad . \quad . \quad . \quad (34)$$

If we now choose δa and δV in such a way that the pressure does not change, so that $dP = 0$, then follows:

$$0 = \left(\frac{dP}{da}\right)_V + \left(\frac{dP}{dV}\right)_\alpha \cdot \left(\frac{dV}{da}\right)_P \quad . \quad . \quad . \quad . \quad (35)$$

With the aid of this (33) passes into (30). As $(dP/dV)a$ is always negative or zero, it follows:

III^c with the absorption of an equal quantity of water the O.W.A. in III^a will generally decrease more than (and in special cases as much as) the O.W.A. in III^b.

The change of the O.W.A. of a liquid or vapour.

Before applying these considerations to an arbitrary equilibrium, we shall first discuss the change of the O.W.A. of a single homogeneous phase, viz. of a liquid or vapour.

When a liquid (vapour) takes in water, the pressure remaining constant, we may assume that its volume will increase; when this liquid (vapour) takes in water, the volume remaining constant, its pressure will increase. So for a liquid (vapour) obtains:

$$\left(\frac{dV}{da}\right)_P > 0 \quad \text{and} \quad \left(\frac{dP}{da}\right)_V > 0 \quad . \quad . \quad . \quad . \quad . \quad (36)$$

It now follows from (20) and also from II^a and II^b:

IV^a when we increase the pressure of a liquid or vapour, its O.W.A. decreases.

IV^b when we diminish the volume of a liquid or vapour, its O.W.A. decreases.

It is clear that these two results follow immediately from one another at once; the relation between both these changes has been determined by (21).

When we apply III^a, III^b and (30) to a liquid or a vapour, we find:

V^a when a liquid or a vapour (P const.) takes in water, its O.W.A. decreases.

V^b when a liquid or a vapour (V const.) takes in water, its O.W.A. decreases.

V^c with an absorption of the same quantity of water the O.W.A. in V^b decreases more than in V^a.

We may also deduce V^b and V^c in the following way.

1. We first cause a liquid (vapour) to take in water, its pressure remaining constant; then its O.W.A. will decrease according to V^a.

2. this liquid (vapour) has increased its volume; if by increase of pressure we reduce this greater volume once more to the original volume, the O.W.A. will decrease again according to IV^a.

So in V^b there are two causes, which diminish the O.W.A., namely the absorption of the water and the increase of pressure; from this it not only follows that the O.W.A. decreases in V^b, but also that it will decrease more in V^b than in V^a.

If we represent the Th. d. pot. of one quantity of liquid (vapour) by ζ, we have for n quantities: $Z = n\zeta$. When these n quantities take in δa mol. water under constant pressure, we have:

$$dZ = (n + \delta a)\left(\zeta + \frac{d\zeta}{dw} dw\right) - n\zeta \quad . \quad . \quad . \quad . \quad (37)$$

Herein $\frac{\delta\zeta}{dw} dw$ represents the total (not the partial) change of the ζ when the W-amount of the liquid changes with δw and the ratio of the amounts of other substances remains constant; we shall refer to this later on. If we represent the W-amount of the liquid (vapour) by w, we have:

$$dw = \frac{nw + \delta a}{n + \delta a} - w = \frac{1 - w}{n + \delta a} \cdot \delta a \quad . \quad . \quad . \quad . \quad (38)$$

(37) now passes into:

$$dZ = \left[\zeta + (1 - w)\frac{d\zeta}{dw}\right]\delta a \quad . \quad . \quad . \quad . \quad . \quad (39)$$

From this follows:

$$\xi = -\xi - (1 - w)\frac{d\zeta}{dw} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

If we represent by ψ the free energy of one quantity of liquid (vapour), we have for the total free energy ψ_t of n quantities: $\psi_t = n\psi$. When these n quantities take in δa mol. water, we have:

$$d\psi_t = (n + \delta a)\left(\psi + \frac{\partial\psi}{\partial v} dv + \frac{d\psi}{dw} dw\right) - n\psi \quad . \quad . \quad (41)$$

in which dv is the change of the volume v of one quantity of liquid (vapour). If we keep the total volume constant, then is:

$$(n + \delta a)(v + dv) = nv \quad . \quad . \quad . \quad . \quad . \quad (42)$$

From this follows:

$$dv = -\frac{v}{n + \delta a} \cdot \delta a \quad . \quad . \quad . \quad . \quad . \quad (43)$$

With the aid of (38) and (43), (41) passes into:

$$d\psi_t = \left[\psi - v\frac{\partial\psi}{\partial v} + (1 - w)\frac{d\psi}{dw}\right]\delta a \quad . \quad . \quad . \quad (44)$$

From this follows:

$$\xi = -\psi + v\frac{\partial\psi}{\partial v} - (1-w)\frac{d\psi}{dw} . \quad \text{. . . . .} \quad (45)$$

As

$$\frac{\partial\psi}{\partial v} = -P \quad \text{and} \quad \left(\frac{d\psi}{dw}\right)_v = \left(\frac{d\zeta}{dw}\right)_P . \quad \text{. . . .} \quad (46)$$

it follows that (40) and (45) are equal, which is also in accordance with (13). From (40) follows:

$$\left(\frac{d\xi}{da}\right)_P = -(1-w)\frac{d^2\xi}{dw^2}\cdot\frac{dw}{da} \quad \text{. . . . . .} \quad (47)$$

which with the aid of (38) passes into:

$$\left(\frac{d\xi}{da}\right)_P = -\frac{(1-w)^2}{n}\cdot\frac{d^2\zeta}{dw^2} . \quad \text{. . . . . .} \quad (48)$$

from which also follows what has been said in IV.

If we represent the composition of a liquid or a vapour by:

$$x\,mol\,X + y\,mol\,Y + \ldots + w\,mol\,W \quad \text{. . . .} \quad (49)$$

in which $w = 1 - x - y \ldots$, then is:

$$\frac{d\zeta}{dw} = \frac{d\zeta}{dx}\cdot\frac{dx}{dw} + \frac{d\zeta}{dy}\cdot\frac{dy}{dw} + \ldots \quad \text{. . . . .} \quad (50)$$

As with this change of the W-amount the ratio of the amounts of the other substances remains constant, we find:

$$\frac{dx}{dw} = -\frac{x}{1-w} \quad ; \quad \frac{dy}{dw} = -\frac{y}{1-w} ; \text{ etc.} \quad \text{. . . .} \quad (51)$$

If we substitute these values in (50) then (40) passes into:

$$\xi = -\zeta + x\frac{d\zeta}{dx} + y\frac{d\zeta}{dy} + \ldots \quad \text{. . . . .} \quad (52)$$

which is in accordance with the values of the O.W.A. of a liquid or a vapour, found previously.

(*To be continued*).

Leiden, Lab. of Inorg. Chemistry.