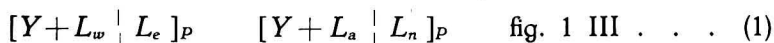


**Chemistry.** — *Equilibria in systems in which phases, separated by a semi-permeable membrane. XIX.* By F. A. H. SCHREINEMAKERS.

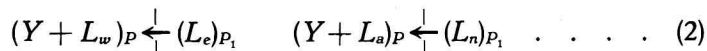
(Communicated at the meeting of February 26, 1927).

*Influence of the pressure on osmotic systems.*

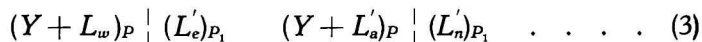
Of the many cases, which may occur, if we change the pressure of an osmotic system in which also occur solid phases, we only shall discuss some cases. If we assume that the saturationcurve  $wv$  and the isotonic curves  $wm$  and  $an$  of fig. 1 (communication III) are valid for the pressure  $P$  then we have a.o. the osmotic equilibria:



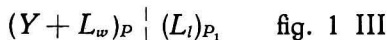
We now bring the pressure on the right side of the membrane on the higher pressure  $P_1$ . As, like we have seen in the previous communication, then the *O.W.A.* of the liquid at the right side of the membrane decreases, we get the osmotic systems:



in which the water diffuses in the direction of the arrows. We now assume that a sufficient quantity of  $Y$  is present, so that the system at the left side of the membrane remains. Then the systems (2) pass into the osmotic equilibria:

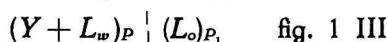


With the isotonic curve of the pressure  $P$  is conjugated an isotonic curve of the pressure  $P_1$ , which must be situated further from the point  $W$  than curve  $wm$ ; we imagine this to be represented by curve  $bo$ . (fig. 1. III). Consequently liquid  $L'_e$  will be represented by the point of intersection  $l$  of the line  $We$  with this curve  $bo$ . The first of the osmotic equilibria (3) becomes, therefore:



The result of increase of pressure is, therefore, that from liquid  $L_e$  so much water diffuses to the left, till it passes into the liquid  $L_l$ .

The composition of the liquids  $L'_a$  and  $L'_n$  in the second of the systems (3) depends on the ratio of the phases. However, it is sure that  $L'_a$  will be represented by a point of the saturationcurve between  $w$  and  $a$  or by the point  $w$  itself. In the latter case  $L'_n$  is represented by point  $o$ ; the second of the osmotic equilibria (3) becomes then:



If, however,  $L'_a$  is represented by a point  $a'$  between  $w$  and  $a$ , then  $L'_n$  will be represented by a point  $n'$  on the side  $WX$  between  $o$  and  $X$ . Those points  $a'$  and  $n'$ , however, are situated not arbitrarily with respect to one another, but the isotonic curve of the pressure  $P$  going through point  $a'$  and the isotonic curve of the pressure  $P_1$  going through point  $n'$  must be conjugated with one another.

We imagine in fig. 1 III two points  $q$  and  $r$  anywhere within the region  $wmXv$ ; as the *O.W.A.* of each of those liquids  $L_q$  and  $L_r$  is larger than that of the solid substance  $Y$  under the same pressure, consequently an osmotic complex

$$[L_q \mid Y \mid L_r]_P \dots \dots \dots (4)$$

exists, in which no diffusion of water occurs. [For systems with two membranes, compare Comm. X]. We are able now, by bringing the pressure of the left liquid to a definite value  $P_1$  and that of the right liquid to a definite value  $P_2$ , to make the *O.W.A.* of both liquids equal to that of the solid substance  $Y$  under the pressure  $P$ . Then the osmotic complex (4) passes into an osmotic equilibrium, which, if we raise the pressure of both liquids still with  $\Delta P$ , passes into the osmotic system:

$$(L_q)_{P_1+\Delta P} \begin{array}{c} \downarrow \\ \rightarrow \\ \uparrow \end{array} Y_P \begin{array}{c} \leftarrow \\ \downarrow \\ \uparrow \end{array} (L_r)_{P_2+\Delta P} \dots \dots \dots (5)$$

in which the water diffuses from left and right towards the solid substance  $Y$ . The double-membrane  $\mid Y \mid$  in system (4) impermeable for water, becomes permeable, therefore, if we raise the pressure of both liquids sufficiently only.

If a sufficient quantity of solid  $Y$  is present, then between the two membranes the system  $Y + L_w$  is formed, and the right and the left liquid lose water as long as their *O.W.A.* becomes equal to that of the liquid  $L_w$  under the pressure  $P$ .

We take under the pressure  $P$  an equilibrium

$$E = (F + L)_P \dots \dots \dots (6)$$

in which  $F$  is an arbitrary liquid. We now bring the pressure to  $P + dP$ ; keeping the total composition of this system  $E$  constant; then we get the new system:

$$E' = (F + L')_{P+dP} \dots \dots \dots (7)$$

in which the liquid  $L'$  differs a little in composition from  $L$ ; this difference in composition is completely defined by the change in pressure  $dP$ . With the transition of system  $E$  into  $E'$  the *O.W.A.* changes, as well on account of the change in pressure itself, as on account of the

change of the composition of the liquid; both influence may intensify or debilitate each other. In the previous communication we have seen that this total change  $d\xi$  of the *O.W.A.* is defined by:

$$d\xi = - \Delta V_E \cdot dP \quad . . . . . (8)$$

if viz.  $\Delta V_E \cdot \delta w$  is the change in volume, which occurs in the system  $E$  under the constant pressure  $P$ , if we add  $\delta w$  quantities of water. As  $\Delta V_E$ , like we will see further, can be positive, negative and also zero, it follows from (8):

the *O.W.A.* of an equilibrium  $E = F + L$  of constant composition decreases or increases at increase of pressure, according as  $\Delta V_E$  is positive or negative; if  $\Delta V_E = 0$ , then the *O.W.A.* does not change with a small increase of pressure.

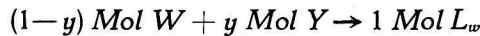
We will determinate for some cases this change of the *O.W.A.* Let us firstly take the equilibrium:

$$E = (Y + L_w)_P \quad \text{fig. 1 III} \quad . . . . . (9)$$

On increase of pressure this passes into the equilibrium:

$$E' = (Y + L'_w)_{P+dP}$$

in which  $L'_w$  is represented by a point  $w'$  which we must imagine in fig. 1 III in the vicinity of point  $w$  on the side  $WY$ . In order to apply formula (8) we have to determinate  $\Delta V_E$  viz. the change in volume which occurs in system  $E$  (consequently under the constant pressure  $P$ ) on addition of water. If we represent the composition of  $L_w$ , which remains unchanged on addition of water to system  $E$ , by  $y$  Mol  $Y + (1-y)$  Mol  $W$ , then, on addition of water the reaction:



occurs. If we represent the molecular volumina of  $L_w$  and the solid substance  $Y$  by  $V$  and  $V_y$ , then we find for  $\Delta V_E$  and also with the aid of (8) for the change of the *O.W.A.*:

$$\Delta V_E = \frac{V - yV_y}{1 - y} \quad . . (10^a) \quad d\xi = - \frac{V - yV_y}{1 - y} dP \quad . . . (10^b)$$

As we have seen in the previous communication, we can deduce the change of the *O.W.A.* yet also in another way. The *O.W.A.* of the liquid  $L_w$  of equilibrium  $E$  is viz. defined by:

$$\xi = - \zeta + y \frac{\partial \zeta}{\partial y} \quad . . . . . (11)$$

For the *O.W.A.*:  $\xi + d\xi$  of liquid  $L'_w$  of equilibrium  $E$  is valid then:

$$d\xi = \left( - V + y \frac{\partial V}{\partial y} \right) dP + y t dy \quad . . . . . (12)$$

in which, however,  $dy$  is defined by  $dP$ . For the equilibrium  $E$  is true viz :

$$\zeta + (1-y) \frac{\partial \zeta}{\partial y} = \zeta_y \quad . . . . . (13)$$

from which follows for the equilibrium  $E'$  :

$$\left[ V + (1-y) \frac{\partial V}{\partial y} - V_y \right] dP + (1-y) t dy = 0 \quad . . . (14)$$

If we substitute this value of  $dy$  in (13) then we find (10<sup>b</sup>).

As  $1-y$  is always positive, the sign of  $\Delta V_E$  is defined by the sign of the numerator of (10<sup>a</sup>). If  $V > V_y$  then the numerator is always positive; if  $V < V_y$  then the sign depends on the value of  $y$ . With values of  $y$ , which do not differ much from 1, the numerator shall be negative then. We may say, therefore, that in general  $\Delta V_E$  shall be positive, unless  $L_w$  should be a concentrated solution, which is formed from its components with contraction of volume.

In order to give another form to  $\Delta V_E$  in (10<sup>a</sup>) we put :

$$V + (1-y) \frac{\partial V}{\partial y} - V_y = \Delta V_y \quad V - y \frac{\partial V}{\partial y} = \Delta V_w \quad . (15)$$

so that  $\Delta V_y \cdot \delta w$  represents the change in volume of the system  $E$ , when  $\delta w$  quantities of solid  $Y$  dissolve in the liquid;  $\Delta V_w \cdot \delta w$  is the change in volume of the liquid, if this takes in  $\delta w$  quantities of water. We now can write for (10<sup>a</sup>):

$$\Delta V_E = \Delta V_w + \frac{y}{1-y} \Delta V_y \quad . . . . . (16)$$

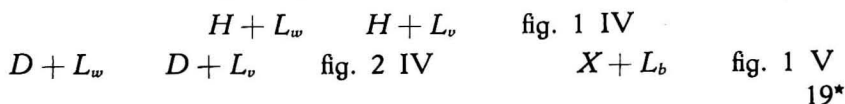
Of the many considerations to which this relation can give rise, we only take the case  $\Delta V_y = 0$ . Instead of (10<sup>a</sup>) and (10<sup>b</sup>) we then get

$$\Delta V_E = \Delta V_w \quad . . (17^a) \quad d\xi = - \Delta V_w \cdot dP \quad . . (17^b)$$

The change of the *O.W.A.* of system  $E$  on change of the pressure is then the same as if no solid  $Y$  but only the liquid  $L_w$  is present. This also follows from (14); if herein  $\Delta V_y = 0$ , then follows  $dy = 0$ , so that the composition of the liquid  $L_w$  remains constant with a change of pressure  $dP$ ; consequently the quantity of solid  $Y$  remains unchanged also.

As the *O.W.A.* of the solid substance  $Y$  under the pressure  $P$  is equal to that of the liquid  $L_w$  of system  $E$ , and under the pressure  $P + dP$  equal to that of the liquid  $L'_w$  of the system  $E'$ , (10<sup>b</sup>), therefore, defines also the change of the *O.W.A.* on a change of pressure of the solid substance  $Y$ .

Of course similar considerations are valid also for the change of the *O.W.A.* on a change of pressure of the equilibria :



and consequently also for the change of the *O.W.A.* on a change of pressure of the solid substances *H*, *D* and *X*.

Hence follows, therefore:

the *O.W.A.* of a solid substance *F* can as well increase as decrease on increase of pressure; this depends on the  $\Delta V_E$  of the system  $E = F + L$ , in which *L* is the liquid, which is formed from the solid substance *F* by taking in (losing) water.

We now take under the pressure *P* the equilibrium:

$$E = (Y + L_a)_P \quad \text{fig. 1 III} \quad \dots \dots \dots (18)$$

and we bring this, while we are keeping constant the total composition, to the pressure  $P + dP$ ; we then get an equilibrium:

$$E' = (Y + L'_a)_{P+dP} \dots \dots \dots (19)$$

in which  $L'_a$  is represented by a point  $a'$ , which we must imagine in fig. 1 III in the vicinity of  $a$  on the line  $Ya$  (within or out of the region  $Ywv$ ). In order to apply formula (8) we have to define  $\Delta V_E$ , viz. the change in volume, which occurs in system (18) on addition of  $\delta w$  quantities of water. However, with this, the composition of the liquid  $L_a$  does not remain constant, as it was the case with liquid  $L_w$  in (9);  $L_a$  viz. changes its composition along curve  $wv$  starting from  $a$  in the direction towards  $w$ .

In order to symplify the calculations, we express the composition of the liquid  $L_a$  in *W*, *Y* and an arbitrary phase *Q*. We write its composition:

$$x \text{ quant. } W + y \text{ quant. } Y + (1 - x - y) \text{ quant. } Q \dots \dots (20)$$

so that we have a system of coordinates with *QW* as *X*-axis and *QY* as *Y*-axis. If the equilibrium *E* consists of *n* quantities of  $L_a$  and *m* quantities of *Y*, then we have:

$$\Delta V_E \cdot \delta w = d(nV + mV_y) = V dn + n \frac{\partial V}{\partial x} dx + n \frac{\partial V}{\partial y} dy + V_y dm \quad (21)$$

in which *V* represents the molecular-volume of the liquid  $L_a$ ;  $dx$  and  $dy$  are the changes in concentration, which occur in the liquid  $L_a$ , by the addition of  $\delta w$  quantities of water. As the quantity of water increases with  $\delta w$ , but the quantity of *Y* and *Q* rests unchanged, it follows from this:

$$\delta w = d(n x) = x dn + n dx \dots \dots \dots (22)$$

$$0 = d(n y + m) = y dn + n dy + dm \dots \dots \dots (23)$$

$$0 = dn(1 - x - y) = dn + dm - \delta w \dots \dots \dots (24)$$

in which (24) is simplified with the aid of (22) and (23). As the liquid  $L_a$  is in equilibrium with solid *Y*, the equation:

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1 - y) \frac{\partial \zeta}{\partial y} = \zeta_y \dots \dots \dots (25)$$

is valid.

Hence follows :

$$[-rx + (1-y)s] dx + [-xs + (1-y)t] dy = 0 \dots (26)$$

Eliminating  $dn$ ,  $dm$ ,  $dx$  and  $dy$  from the equations (21)–(24) and (26) we find the value of  $\Delta V_E$ . This elimination becomes more simple if we let coincide the arbitrary phase Q in (20) with the point  $a$  in fig. 1 III; then  $aW$  is the  $X$ -axis and  $aY$  the  $Y$ -axis of the system of coordinates; we now have  $x=0$  and  $y=0$ . Putting those values in (22)–(24) and in (26) and eliminating  $dn$ ,  $dm$ ,  $dx$  and  $dy$  then we find after dividing by  $\delta w$  :

$$\Delta V_E = V + \frac{\partial V}{\partial x} + \frac{s}{t} \left( V_y - V - \frac{\partial V}{\partial y} \right) \dots (27)$$

so that the change of the  $O.W.A.$  is known with the aid of (8).

We are able to deduce this more plainly in the following way. We represent again the composition of the liquid  $L_a$  as in (20); its  $O.W.A.$  is then defined by

$$\xi = -\zeta - (1-x) \frac{\partial \zeta}{\partial y} + y \frac{\partial \zeta}{\partial y}$$

For an arbitrary liquid, which differs infinitely little from  $L_a$  then is under the pressure  $P + dP$  :

$$d\xi = - \left\{ \begin{aligned} & \left[ V + (1-x) \frac{\partial V}{\partial x} - y \frac{\partial V}{\partial y} \right] dP + \\ & + [-(1-x)r + ys] dx + [-(1-x)s + yt] dy \end{aligned} \right\} (28)$$

If this new substance under the pressure  $P + dP$  is always in equilibrium with solid  $Y$ , then follows from (25) that  $dx$  and  $dy$  must satisfy an equation, which we get by adding to (26) the term :

$$\left[ V - x \frac{\partial V}{\partial x} + (1-y) \frac{\partial V}{\partial y} - V_y \right] dP \dots (29)$$

We call this (26<sup>a</sup>). Just as above we now let coincide the arbitrary phase Q with the point  $a$ . As then  $x$  and  $y$  become zero, (28) and (26<sup>a</sup>) pass into :

$$d\xi = - \left[ V + \frac{\partial V}{\partial x} \right] dP - r dx - s dy \dots (30)$$

$$0 = - \left[ V + \frac{\partial V}{\partial y} - V_y \right] dP + s dx + t dy \dots (31)$$

We now must define  $dx$  and  $dy$  in such a way that liquid  $L_a$  of equilibrium (18) passes into  $L'_a$  of (19); as, like we have noted already above  $L'_a$  must be situated on the line  $aY$ , consequently  $dx=0$ . If we substitute this in (30) and (31) and eliminating then  $dy$  we find :

$$d\xi = - \left[ V + \frac{\partial V}{\partial x} + \frac{s}{t} \left( V_y - V - \frac{\partial V}{\partial y} \right) \right] dP \dots (32)$$

Consequently the same value for  $d\xi$  as follows from (27).

In a similar way we can define the change of the *O.W.A.* in the systems:

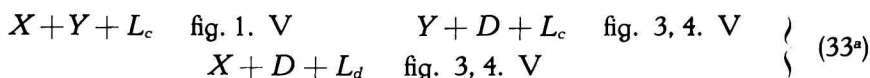


and other systems in which a liquid, saturated with a solid substance.

We now take a liquid, saturated with two solid substances, viz. the equilibrium:

$$E = (F + F_1 + L)_P \dots \dots \dots (33)$$

If we bring this, while its composition remains constant, under the pressure  $P + dP$ , then the liquid  $L$  gets a definite change in composition. If we take as simple example for  $E$  a ternary system, f.i. one of the equilibria:



then, on addition of water, the liquid does not change its composition, so that a phases-reaction occurs. If we represent the composition of the liquid  $L_c$  in the first of the equilibria mentioned above, by:

$$x \text{ Mol } X + y \text{ Mol } Y + (1-x-y) \text{ Mol } W \dots \dots (34)$$

then on addition of water the reaction:



occurs. Hence now follows:

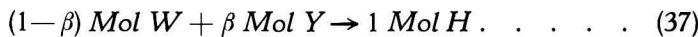
$$\Delta V_E = \frac{V - x V_X - y V_Y}{1-x-y} \dots \dots \dots (35)$$

so that the change of the *O.W.A.* is defined. Corresponding considerations as for (10<sup>a</sup>) are valid for this value of  $\Delta V_E$ .

If we take the system:

$$E = (Y + H + L_d)_P \quad \text{fig. 2. V} \dots \dots \dots (36)$$

then, on addition of water, also herein a phases-reaction occurs in which, however, the liquid  $L_d$  does not participate. If we represent the composition of the hydrate  $H$  by:  $\beta \text{ Mol } Y + (1-\beta) \text{ Mol } W$ , then this reaction is:



Hence follows:

$$\Delta V_E = \frac{V_H - \beta V_Y}{1-\beta} \qquad d\xi = - \frac{V_H - \beta V_Y}{1-\beta} \cdot dP \dots \dots (38)$$

by which the influence of a change in pressure on the *O.W.A.* of system (36) is defined.

We also can deduce this again in the following way. If we bring the pressure of (36) to  $P + dP$  then arises the equilibrium:

$$E' = (Y + H + L_d)_{P+dP} \dots \dots \dots (39)$$

in which  $L'_d$  is represented by a point  $d'$ , which we must imagine in fig. 2 V in the vicinity of point  $d$ . If we represent the composition of the liquid  $L_d$  by (34), then its *O.W.A.* is defined by:

$$\xi = -\zeta + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \dots \dots \dots (40)$$

As the liquid  $L_d$  is saturated with  $Y + H$ , are valid the equations:

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} = \zeta_Y \quad \zeta - x \frac{\partial \zeta}{\partial x} + (\beta - y) \frac{\partial \zeta}{\partial y} = \zeta_H \dots (41)$$

which we write, with the aid of (40) in the form:

$$\xi = \frac{\partial \zeta}{\partial y} - \zeta_Y \quad \xi = \beta \frac{\partial \zeta}{\partial y} - \zeta_H \dots \dots \dots (42)$$

For the liquid  $L'_d$  of equilibrium  $E'$  under the pressure  $P + dP$  is valid then:

$$d\xi = \left( \frac{\partial V}{\partial y} - V_Y \right) dP + s dx + t dy$$

$$d\xi = \left( \beta \frac{\partial V}{\partial y} - V_H \right) dP + \beta (s dx + t dy)$$

from which follows by elimination of  $s dx + t dy$ :

$$d\xi = - \frac{V_H - \beta V_Y}{1 - \beta} \cdot dP \dots \dots \dots (43)$$

which is in accordance with (38).

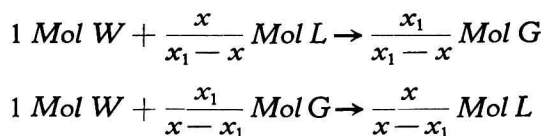
As the systems (33<sup>a</sup>) and (39) define also the *O.W.A.* of the solid complexes  $X + Y$ ,  $Y + D$ ,  $X + D$  and  $Y + H$ , we also know, therefore, the change of the *O.W.A.* of those solid complexes, if we bring their pressure from  $P$  to  $P + dP$ .

We now take under the pressure  $P$  an equilibrium:

$$E = (G + L)_P \dots \dots \dots (44)$$

with a vapour  $G$  and a liquid  $L$ . In order to make the calculation not too extensive, we assume that  $E$  is a binary system. We represent the composition of the vapour by  $x$  Mol  $X + (1-x)$  Mol  $W$  and that of the liquid by  $x_1$  Mol  $X + (1-x_1)$  Mol  $W$ .

As the phases of this binary equilibrium have a constant composition at constant  $T$  and  $P$ , on addition of water, according as  $x_1 - x$  or  $x - x_1$  is positive, occurs one of the reactions:





If we represent the volume of the vapour by  $V$  and that of the liquid by  $V_1$  then follows:

$$\Delta V_E = \frac{x_1 V - x V_1}{x_1 - x} \dots \dots \dots (45)$$

by which is defined the change of the *O.W.A.* of system  $E$  on a change of pressure.

We are able to find this in the following way also.

The *O.W.A.* of the vapour (and consequently also that of the liquid and that of the total system  $E$ ) is defined by:

$$\xi = -\zeta + x \frac{\partial \zeta}{\partial x} \dots \dots \dots (46)$$

If we bring this system under the pressure  $P + dP$ , while its total composition remains constant, then we get the equilibrium:

$$E' = (L' + G')_{P+dP} \dots \dots \dots (47)$$

of which the *O.W.A.* is defined by

$$d\xi = \left( -V + x \frac{\partial V}{\partial x} \right) dP + x r dx \dots \dots \dots (48)$$

and in which  $dx$  has a value defined by  $dP$ . For the equilibrium  $E$  is true viz.:

$$\zeta - x \frac{\partial \zeta}{\partial x} = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} \quad \frac{\partial \zeta}{\partial x} = \frac{\partial \zeta_1}{\partial x_1} \dots \dots \dots (49)$$

from which follow for equilibrium  $E'$  the equations:

$$\begin{aligned} \left( V - x \frac{\partial V}{\partial x} \right) dP - x r dx &= \left( V_1 - x_1 \frac{\partial V_1}{\partial x_1} \right) dP - x_1 r_1 dx_1 \\ \frac{\partial V}{\partial x} \cdot dP + r dx &= \frac{\partial V_1}{\partial x_1} dP + r_1 dx_1 \end{aligned}$$

If we substitute, after having eliminated  $dx_1$ , in (48)  $dx$  then we find:

$$d\xi = \frac{x_1 V - x V_1}{x - x_1} \cdot dP \dots \dots \dots (50)$$

which is corresponding with the value of  $d\xi$  which follows from (45).

In order to define the sign of the coefficient of  $dP$  we distinguish two cases.

1. The vapour  $G$  has a smaller amount of water than the liquid  $L$ ; consequently we have  $1 - x < 1 - x_1$  or  $x > x_1$ . As in general the volume  $V$  of the vapour is many hundred times as large as the volume  $V_1$  of the liquid,  $x_1 V - x V_1$  will be, therefore, generally positive, unless in the special case that  $x$  (viz. the concentration of the substance  $X$  in the vapour) is many hundred times as large as  $x_1$  (the concentration of the substance  $X$  in the liquid).

If we exclude this case, then the coefficient of  $dP$  in (50) is positive, therefore.

2. The liquid  $L$  has a smaller amount of water than the vapour  $G$ ; consequently we have  $1 - x_1 < 1 - x$  or  $x_1 > x$ . The numerator of (50) now always is positive, the denominator negative, so that the coefficient of  $dP$  is negative.

Consequently we can say:

the *O.W.A.* of the binary system  $G + L$  becomes larger on increase of pressure, when the vapour has the smallest amount of water, and smaller if this is the case with the liquid.

We now take the osmotic equilibrium:

$$(Y + L)_P \mid (Y + L)_P \dots \dots \dots (51)$$

in which on both sides of the membrane the system (9) discussed above, under the pressure  $P$ . We distinguish two cases.

1. The solubility of the solid substance  $Y$  increases on increase of pressure.

If we assume that the total concentration of the substance  $Y$  is smaller at the left side of the membrane than on the right side, then, as on increase of pressure the quantity of solid  $Y$  decreases on both sides of the membrane, under a definite pressure  $P_1$  ( $P_1 > P$ ) the solid  $Y$  at the left of the membrane will disappear, while it is still present at the right side; then (51) passes into the osmotic equilibrium:

$$(L_1)_{P_1} \mid (Y + L_1)_{P_1} \dots \dots \dots (52)$$

in which the liquid has the same composition on both sides. If we increase the pressure still with  $\Delta P$ , then the liquid at the left side of the membrane remains unchanged; at the right side of the membrane, however, it gets a somewhat other composition  $L'_1$ . The *O.W.A.* at the left and at the right side of the membrane then increases with:

$$(d\xi)_l = -\Delta V_W \cdot dP \quad (d\xi)_r = -\Delta V_E \cdot dP \dots \dots (53)$$

in which  $\Delta V_W$  and  $\Delta V_E$  are defined by (10<sup>a</sup>), (15) and (16). It now follows from (53):

$$(d\xi)_l - (d\xi)_r = \frac{y}{1-y} \cdot \Delta V_y \cdot dP \dots \dots \dots (54)$$

As the solubility of the substance  $Y$  increases on increase of pressure,  $\Delta V_Y$  must be negative, as is apparent from (14) and (15); consequently follows from (54):

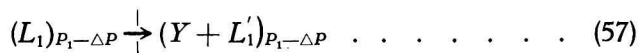
$$(d\xi)_l < (d\xi)_r \dots \dots \dots (55)$$

On an increase of pressure  $\Delta P$  ( $\Delta P > 0$ ) consequently (52) passes into the osmotic system:

$$(L_1)_{P_1+\Delta P} \mid (Y + L'_1)_{P_1+\Delta P} \dots \dots \dots (56)$$

in which the water diffuses in the direction of the arrow; this diffusion continues till the liquid  $L_1$  gets the composition  $L'_1$ .

2. The solubility of the solid substance  $Y$  decreases on increase of pressure. Then we must decrease the pressure, in order to make disappear the solid substance  $Y$  from the system  $Y + L$ ; the osmotic equilibrium (52) then arises under a pressure  $P_1$  smaller than  $P$ . As  $\Delta V_y$  in (54) is positive on a decreased of pressure  $\Delta P$  [in (54) then is  $dP = -\Delta P$ ] (52) passes into the osmotic system:



in which the water diffuses in the same manner from left to right; the water-diffusion continues also here till the liquid  $L_1$  gets the composition  $L'_1$ .

(To be continued.)

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