

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

(Communicated at the meeting of November 27, 1926).

Influence of the pressure on osmotic systems.

We take a system E_P (of one or more phases) under the pressure P . We bring this system, while its temperature and total composition remain constant, under the pressure $P + dP$. Then a new system E'_{P+dP} arises, in which the phases can differ a little in composition with those of the first system; this difference in composition is defined by the value of dP .

In order to compare the O.W.A. of the two systems:

$$E_P \qquad E'_{P+dP}$$

we represent the total thermodynamical potential of the first system by Z and that of the second system by Z' . We then have:

$$Z' = Z + VdP. \quad \dots \quad (1)$$

in which V represents the total volume of system E under the pressure P . The O.W.A. of the first system is defined by:

$$\varphi = \frac{\partial Z}{\partial w} \quad \dots \quad (2)$$

if viz. $\frac{\partial Z}{\partial w} \cdot \delta w$ represents the change of the thermodynamical potential, which the first system receives, if this takes in δw quantities of water. The O.W.A. of the second system now is:

$$\varphi' = \frac{\partial Z'}{\partial w} = \frac{\partial Z}{\partial w} + \frac{\partial V}{\partial w} \cdot dP \quad \dots \quad (3)$$

We now put:

$$\frac{\partial V}{\partial w} = \Delta V_E$$

Hence is apparent that $\Delta V_E \cdot \delta w$ represents the change, which gets the total volume V of system E , if this takes in δw quantities of water. If we put further $\varphi' = \varphi + d\varphi$ then (3) passes into:

$$d\varphi = \Delta V_E \cdot dP. \quad \dots \quad (4)$$

by which the change of the O.W.A. is defined. We can also deduce (4) at once from (2) by differentiating this with respect to P .

As φ and the *O.W.A.* of a system change in opposite direction, we shall substitute in the following φ by $-\xi$; then the ξ and the *O.W.A.* of a system change in the same direction; then they become viz. at the same time larger or smaller. Consequently we may write instead of (2) and (4)

$$\xi = -\varphi = -\frac{\partial Z}{\partial w} \quad (5^a) \qquad d\xi = -d\varphi = -\Delta V_E \cdot dP \quad (5^b)$$

It follows from (5^b):
the *O.W.A.* of a system E becomes smaller on increase of pressure, if ΔV_E is positive, and larger if ΔV_E is negative.

If we indicate by an arrow the direction, in which the water diffuses, then we can express this in the following way:

$$\Delta V_E > 0 \qquad E_P \leftarrow E_{P+\Delta P} \quad \dots \quad (6^a)$$

$$\Delta V_E < 0 \qquad E_P \rightarrow E_{P+\Delta P} \quad \dots \quad (6^b)$$

in which E_P represents the system under the pressure P and $E_{P+\Delta P}$ this same system under the pressure $P + \Delta P$, and in which ΔP is positive.

If both the systems E_1 and E_2 have the same *O.W.A.* under the pressure P , then we have the osmotic equilibrium:

$$(E_1)_P \mid (E_2)_P \quad \dots \quad (7^a)$$

If we raise the pressure to $P + dP$ then both systems will have no more the same *O.W.A.*; that of the left system will increase with:

$$d\xi_1 = -\Delta V_{E_1} \cdot dP$$

and that of the right system with:

$$d\xi_2 = -\Delta V_{E_2} \cdot dP$$

If we take $\Delta V_{E_1} > \Delta V_{E_2}$ then, on increase of pressure, the *O.W.A.* of the right system becomes greater than that of the left system; consequently water will diffuse from left to right. We can represent this by:

$$\Delta V_{E_1} > \Delta V_{E_2} \qquad (E_1)_{P+\Delta P} \rightarrow (E_2)_{P+\Delta P} \quad \dots \quad (7^b)$$

in which ΔP is positive. Consequently we may say:

if we increase the pressure of an osmotic equilibrium, then the water diffuses in such direction that contraction of volume occurs.

We can deduce also in another way the influence of a change in pressure on the *O.W.A.* of a system. In previous communications (f.i. in Comm. VI) we have seen a.o. that the *O.W.A.* of a system E :

in which one or more liquids occur, is equal to the *O.W.A.* of each of those liquids;

in which by taking in — or losing a little water a liquid arises, is equal to the *O.W.A.* of this liquid ;

in which by taking in — or losing water a phases-reaction occurs, is equal to the *O.W.A.* of a liquid with which that system can be in equilibrium.

The same is true also for systems with a vapour or for those which can be in equilibrium with a vapour.

If we represent the composition of the liquid or vapour, above-mentioned, by :

$$xX + yY + zZ + \dots + (1-x-y-z \dots) W. \dots (8^a)$$

or f.i. by :

$$wW + xX + yY + \dots + (1-w-x-y \dots) Q \dots (8^b)$$

in which *X, Y* etc. (except *W*) may be components or composants, then the *O.W.A.* of the system *E* is, therefore, defined by :

$$\xi = -\varphi = -\zeta + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} + \dots \dots \dots (9^a)$$

$$\xi = -\varphi = -\zeta - (1-w) \frac{\partial \zeta}{\partial w} + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \dots \dots \dots (9^b)$$

If we bring the system *E* from the pressure *P* to *P + dP* then the *O.W.A.* of this system changes with :

$$d\xi = \frac{\partial \xi}{\partial P} \cdot dP + \frac{\partial \xi}{\partial x} \cdot dx + \frac{\partial \xi}{\partial y} \cdot dy + \dots \dots \dots (10)$$

It now depends on the number of freedoms of the system *E* whether *dx dy* etc. are completely defined by the change in pressure *dP*; if this is not the case, then we can put still different conditions, which must be satisfied by the changes of the system.

In order to apply those general considerations to some simple cases, we take the systems :

$$E = G \text{ (11}^a) \qquad E = L \dots \dots \dots (11^b)$$

which consist each of one phase only; the change of the *O.W.A.* at a change of pressure is defined by (5^b). For system (11^a) $\Delta V_E \cdot \delta w$ now represents the increase of volume, which gets one quantity of vapour, if this takes in δw quantities of water; for system (11^b) it is the increase of volume if one quantity of liquid takes in δw quantities of water. This increase of volume is positive for vapours and also in general for liquids, excepted in the special case that the contraction occurring with the mixture would be still greater than the volume of the taken δw quantities of water. In the following, unless the opposite is precisely said, we shall take this increase of volume positive. We then find :

the O.W.A. of a vapour and that of a liquid becomes smaller on increase of pressure and larger on decrease of pressure.

In the osmotic systems:

$$G_P \leftarrow G_{P+\Delta P} \quad (12^a) \quad L_P \leftarrow L_{P+\Delta P} \quad \dots \quad (12^b)$$

the water diffuses, therefore, in the direction of the arrows [compare also system (6^a)].

In order to express the change in volume ΔV_E , mentioned above, we take a vapour G or liquid L of the composition:

$$x \text{ Mol } X + y \text{ Mol } Y + (1-x-y) \text{ Mol } W \quad \dots \quad (13)$$

with the volume V . If we mix this with δw quantities of water, then arise $1 + \delta w$ quantities of a new vapour or liquid, which differs infinitely little (dx and dy) in composition from the original. Consequently we have:

$$\Delta V_E \cdot \delta w = (1 + \delta w) \left(V + x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} \right) - V \quad \dots \quad (14)$$

For dx and dy we find:

$$dx = \frac{x}{1 + \delta w} - x = \frac{-x \cdot \delta w}{1 + \delta w} \quad dy = \frac{y}{1 + \delta w} - y = \frac{-y \cdot \delta w}{1 + \delta w} \quad (15)$$

If we substitute those values in (14), then follows:

$$\Delta V_E = V - x \frac{\partial V}{\partial x} - y \frac{\partial V}{\partial y} \quad \dots \quad (16)$$

the second part of which in the case of a vapour, which follows the gas-laws, passes into the volume V of that vapour.

We are able to deduce this also in the following way, The O.W.A. of a vapour or liquid (13) is defined by:

$$\xi = -\varphi = -\zeta + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \quad \dots \quad (17)$$

Hence follows, in connection with the value of ΔV_E from (16):

$$d\xi = -\Delta V_E dP + (rx + sy) dx + (sx + ty) dy \quad \dots \quad (18)$$

If we keep constant the composition of this vapour or liquid, so that dx and dy are zero, then (18) passes into (5^b).

As we can give still arbitrary values to dx and dy in (18), we choose them in such a way, that the new system E' arises from E by taking in or losing a little water. We then have to put:

$$dx : x = dy : y = d\lambda \quad \dots \quad (19)$$

so that $d\lambda$ is positive if the liquid or vapour loses water. With the aid of (19) now (18) passes into:

$$d\xi = -V_E dP + (rx^2 + 2sxy + ty^2) d\lambda \quad \dots \quad (20)$$

We define the system E' in such a way that its *O.W.A.* under the pressure $P + dP$ is equal to that of system E under the pressure P . As then $d\xi$ must be zero, follows from (20)

$$d\lambda = \frac{V_E}{rx^2 + 2sxy + ty^2} dP \dots \dots \dots (21)$$

in which the denominator, as long as we consider stable states, is positive. As, therefore, $d\lambda$ and dP have the same sign, it follows :

if we increase the pressure of a liquid or vapour with a definite amount dP , then this must lose a definite quantity of water, in order to keep the same *O.W.A.*

We take a liquid c of fig. 1 under the pressure P ; all liquids, which have under this same pressure the same *O.W.A.* as this liquid L_c are situated on the isotonic curve acb going through point c . If we take the same liquid L_c under a pressure $P + dP$, then all liquids which have the same *O.W.A.* under this pressure $P + dP$ as L_c , will be situated also on an isotonic curve a_1cb_1 going through point c , which curve, as follows from the previous considerations, does not coincide with acb .

If we take viz. an arbitrary liquid q of curve acb , then this is isotonic with L_c under the pressure P ; consequently we have the osmotic equilibrium :

$$(L_c)_P \mid (L_q)_P \dots \dots \dots (22)$$

If we represent the increase of volume of the liquids L_c and L_q when

taking in δw quantities of water, by $\Delta V_c \cdot \delta w$ and $\Delta V_q \cdot \delta w$, then, if we bring the pressure of (22) to $P + dP$, the *O.W.A.* of the left system increases with $-\Delta V_c \cdot dP$ and that of the right system with $-\Delta V_q \cdot dP$. As ΔV_c and ΔV_q are different in general, L_c and L_q are no more isotonic, therefore, under the pressure $P + dP$. The isotonic curve of the pressure $P + dP$ which goes through the point c must be therefore, an other than that of the pressure P .

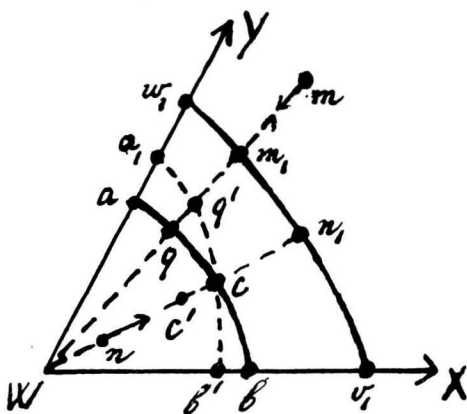


Fig. 1.

We are able to show this also in the following way. For the osmotic equilibrium (22) is true :

$$\left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \right)_c = \left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \right)_q \dots \dots \dots (23)$$

For an osmotic equilibrium :

$$(L_c)_{P+dP} \mid (L_q)_{P+dP} \dots \dots \dots (24)$$

in which L'_q represents a liquid, which differs infinitely little (dx and dy) from L_q then follows from (23):

$$\Delta V_c \cdot dP = \Delta V_q \cdot dP - (rx + sy)_q dx - (sx + ty)_q dy \quad . \quad (25)$$

If we choose L'_q in such a way that it is represented by a point q' (fig. 1) on the line Wq then dx and dy satisfy (19); (25) now passes into:

$$(rx^2 + 2sxy + ty^2)_q d\lambda = (\Delta V_q - \Delta V_c) \cdot dP \quad . \quad . \quad (26)$$

$(\Delta V_q - \Delta V_c) \delta w$ is the change in volume if δw quantities of water diffuse from L_c towards L_q . As in general this change is not zero, $d\lambda$, therefore, has a value, different from zero. If $d\lambda$ is positive, then point q' is situated as is drawn in fig. 1.

If L_q proceeds along the curve acb , then the value of $\Delta V_q - \Delta V_c$ changes; if q coincides with c , then this value is zero of course. If we take this value positive, if q is situated between a and c and negative if q is situated between c and b , then we can represent the isotonic curve of the pressure $P + dP$ ($dP > 0$) by $a_1 c b_1$. For small values of dP those curves acb and $a_1 c b_1$ have the same direction with approximation in the point c .

Above we have seen that both the liquids of (22) are no more in equilibrium with one another under a pressure $P + \Delta P$. If we keep constant the total composition, then, as we have deduced already above in general for system (7^a) in (7^b), the water will diffuse under the pressure $P + \Delta P$ in such direction that the total volume decreases. If we take $\Delta V_q > \Delta V_c$ then a little water must diffuse, therefore, from L_q towards L_c ; we shall represent this, just as in (7^b) by:

$$\Delta V_q > \Delta V_c \quad (L_c)_{P+\Delta P} \leftarrow (L_q)_{P+\Delta P} \quad . \quad . \quad . \quad (27)$$

Under the pressure $P + \Delta P$ a new osmotic equilibrium:

$$(L'_c)_{P+\Delta P} \mid (L'_q)_{P+\Delta P} \quad . \quad . \quad . \quad . \quad (28)$$

is formed, therefore.

If we represent the liquids of this latter osmotic equilibrium in fig. 1 by c' and q' , then the line $q'c'$ must go through the point (situated on the line cq) which represents the complex of the liquids L_q and L_c . The position of the points q' and c' depends, therefore, not only on the value of dP , but also on the ratio of the quantities of the two liquids. We can deduce this also as follows.

For the osmotic equilibrium (22) equation (23) is valid; for an osmotic equilibrium (28), of which pressure and composition of the liquids differ a little from (22) then is valid:

$$\Delta V_c \cdot dP - (rx + sy)_c \cdot dx_c - (sx + ty)_c \cdot dy_c = \left. \begin{aligned} & \\ & \end{aligned} \right\} \quad . \quad . \quad (29)$$

$$= \Delta V_q \cdot dP - (rx + sy)_q \cdot dx_q - (sx + ty)_q \cdot dy_q \left. \begin{aligned} & \\ & \end{aligned} \right\}$$

In our case we have to define in such a way the changes of the concentrations: dx_c etc., that L'_c arises from L_c by taking in δw quan-

tities of water and L'_q from L_q by giving δw quantities of water (δw positive or negative). If there are n quantities of L_c and m quantities of L_q then we find:

$$\left. \begin{aligned} dx_c &= -\frac{x_c}{n} \cdot \delta w & dy_c &= -\frac{y_c}{n} \cdot \delta w \\ dx_q &= +\frac{x_q}{m} \cdot \delta w & dy_q &= +\frac{y_q}{m} \cdot \delta w \end{aligned} \right\} \dots \dots \dots (30)$$

If we substitute those values in (29) and if we put:

$$(x^2r + 2 xys + y^2 t)_c = K_c \qquad (x^2r + 2 xys + y^2 t)_q = K_q$$

then follows:
$$\left(\frac{K_c}{n} + \frac{K_q}{m} \right) \delta w = (\Delta V_q - \Delta V_c) dP \dots \dots \dots (31)$$

so that δw has the same sign as dP . In accordance with (27) we find, therefore, that for positive values of dP the water diffuses from L_q towards L_c , (31) defines, however, also δw and in accordance with (30), therefore, also dx_c etc., as function of the quantities n and m of both the liquids.

If we take infinitely large the quantity of L_c in (22) then its composition rests unchanged when taking in δw quantities of water; equilibrium (28) then is the same as (24). As n becomes infinitely large, $K_c : n$ in (31) becomes zero, therefore, and as $\delta w : m$ in (31) is equal to $d\lambda$ in (26), then (31) passes into (26).

In the osmotic equilibrium

$$(W)_P \mid (L_1)_{P_1} \text{ (fig. 1) } \dots \dots \dots (32)$$

we find at the left side of the membrane pure water under the pressure P and at the right side of the membrane a liquid L_1 under the pressure P_1 . In this special case, therefore, $\pi = P_1 - P$ is the osmotic pressure of the liquid L . The osmotic equilibrium (32) is defined by:

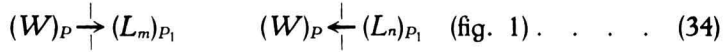
$$(\zeta w)_P = \left(\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \right)_{P_1} \dots \dots \dots (33)$$

If we consider stable states only: then we can show in a similar way as f.i. in communication I that (33) can be satisfied only if $P_1 > P$. We now give a definite value to both pressures; then it follows from (33) that the liquids L_1 of (32) are represented by a curve, f. i. curve $w_1 v_1$ in fig. 1.

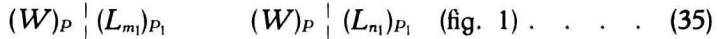
As under this pressure P_1 all liquids of the region $Ww_1 v_1$ have a smaller *O.W.A.* than the liquids of curve $w_1 v_1$ under this same pressure P_1 and as those of the region $w_1 v_1 XY$ have a greater *O.W.A.* than the liquids of curve $v_1 w_1$, it follows, therefore:

- under a pressure $P_1 > P$ all liquids
- of curve $w_1 v_1$ have the same,
- of region $Ww_1 v_1$ have a smaller,
- and of region $w_1 v_1 XY$ have a greater,
- O.W.A.* than that of pure water under the pressure P .

If we take, therefore, the osmotic systems:



then in the first system the water diffuses from the pure water towards the liquid; in the second system, however, water diffuses from the liquid towards the pure water; the liquids m and n move in fig. 1, therefore, in the direction of the arrows, till they reach curve $w_1 v_1$ (if in the first of those systems a sufficient quantity of pure water is present). Then the systems (34) pass into the osmotic equilibria:



We now take in fig. 2, in which $w_1 v_1$ represents the corresponding curve of fig. 1, a liquid L of curve ab . If ab is an isotonic curve of the pressure P , then all liquids of this curve ab have the same *O.W.A.* under the pressure P . If we replace in (32) the pure water by this liquid L , then an osmotic equilibrium:



arises, in which of course the liquids L_1 now must have an other composition than in (32). As the *O.W.A.* of the liquids of curve ab under the pressure P is greater than that of the pure water under this same pressure, curve $a_1 b_1$ which represents the liquids L_1 of (36) must be situated in fig. 2 further from the point W than curve $w_1 v_1$.

Every arbitrary liquid L of curve ab has, therefore, under the pressure

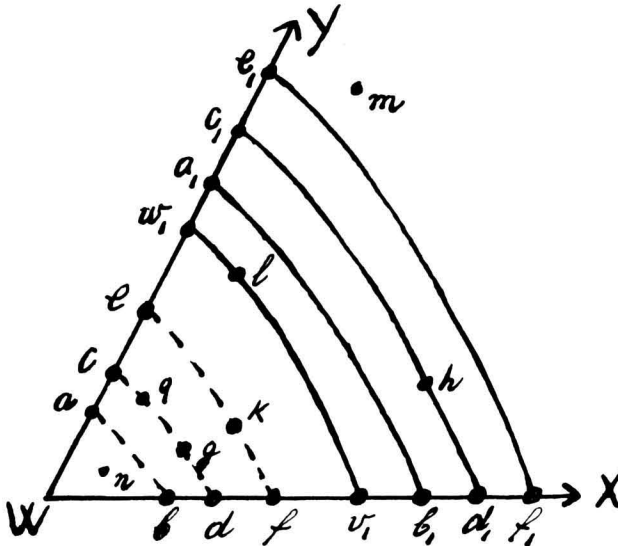


Fig. 2.

P the same *O.W.A.* as every arbitrary liquid of curve $a_1 b_1$ under the pressure P_1 ; we may call those curves ab and $a_1 b_1$ conjugated isotonic curves of the pressures P and P_1 . The same is true for the curves cd

and $c_1 d_1$, for ef and $e_1 f_1$ etc. Consequently we find in fig. 2 a.o. the osmotic equilibria:

$$\begin{array}{ccc} (W)_P \mid (L_i)_{P_1} & (L_a)_P \mid (L_{a_1})_{P_1} & (L_a)_P \mid (L_{b_1})_{P_1} \\ (L_g)_P \mid (L_h)_{P_1} & (L_q)_P \mid (L_{d_1})_{P_1} & (L_k)_P \mid (L_{f_1})_{P_1} \end{array}$$

If we consider two conjugated isotonic curves of the pressures P and P_1 f.i. the curves cd and $c_1 d_1$ then follows from this:

- under a pressure $P_1 > P$ all liquids
- of the isotonic curve $c_1 d_1$ have the same
- of the region $W_{c_1 d_1}$ have a smaller
- and of the region $c_1 d_1 XY$ have a greater
- $O.W.A.$ than the liquids of curve cd under the pressure P .

Hence follows that in the osmotic system:

$$(L_g)_P \xrightarrow{\mid} (L_m)_{P_1} \quad (\text{fig. 2}) \dots \dots \dots (37)$$

the water must diffuse from left to right. It now depends on the ratio of the quantities of both liquids on which conjugated isotonic curves the equilibrium will be formed. If this is the case f.i. on the curves ef and $e_1 f_1$ then is formed the osmotic equilibrium:

$$(L'_g)_P \mid (L'_m)_{P_1} \quad (\text{fig. 2}) \dots \dots \dots (38)$$

in which the left liquid in fig. 2 is represented by the point of intersection of the line Wg with curve ef and the right liquid by the point of intersection of Wm with $e_1 f_1$.

This conversion of (37) into (38) is possible, of course, only then, when the complex of the liquids L_g and L_m is situated within the region $eff_1 e_1$; if this is not the case, then the system (37) also can not be formed on the curves ef and $e_1 f_1$.

We now take the osmotic systems:

$$\left. \begin{array}{cc} (L_g)_P \mid (L_g)_P & (L_g)_P \mid (L_q)_P \\ (L_g)_P \xrightarrow{\mid} (L_i)_P & (L_g)_P \xleftarrow{\mid} (L_n)_P \end{array} \right\} (\text{fig. 2}) \dots \dots (39)$$

in which in all at the left side of the membrane the liquid L_g is present; the pressure is equal on both sides of the membrane, viz. P . It appears from fig. 2 that both the first systems then form osmotic equilibria, in the third system the water diffuses towards the right and in the last system towards the left.

If, however, we bring at the right side of the membrane the pressure from P to P_1 then all liquids, at the right side of the membrane are situated within the region $W_{c_1 d_1}$ of fig. 2; consequently they have all a smaller $O.W.A.$ than the liquid L_g under the pressure P . Instead of (39) we then get the systems:

$$\left. \begin{array}{cc} (L_g)_P \xleftarrow{\mid} (L_g)_{P_1} & (L_g)_P \xleftarrow{\mid} (L_q)_{P_1} \\ (L_g)_P \xleftarrow{\mid} (L_i)_{P_1} & (L_g)_P \xleftarrow{\mid} (L_n)_{P_1} \end{array} \right\} (\text{fig. 2}) \dots \dots (40)$$

in which the water diffuses towards the left. If the ratio of the quantities of both liquids in each of those systems is chosen in such a way, that the equilibrium is formed on the conjugated isotonic curves ab and a_1b_1 , then the left liquid is represented by the point of intersection of the line Wg with curve ab ; the right liquids are represented by the points of intersection of the lines Wg, Wq, Wl and Wn with curve a_1b_1 .

We now take the osmotic equilibrium:

$$(G)_P \mid (G_1)_P \dots \dots \dots (41)$$

in which on both sides of the membrane a vapour under the pressure P . If we bring the pressure on both sides of the membrane to $P + \Delta P$, then [comp (7^a) and (7^b)] the water must diffuse in such direction, that the total volume decreases. If, however, those vapours, follow the gas-laws, then the total volume does not change at diffusion of water, consequently (41) passes, without diffusion occurs, into the osmotic equilibrium,

$$(G)_{P+\Delta P} \mid (G_1)_{P+\Delta P} \dots \dots \dots (42)$$

This appears still also as follows. In the previous communication we have seen that two vapours are in osmotic equilibrium, when the partial vapour-pressure of the water-vapour is equal in both. If this is the case under the pressure P then this is also the case under the pressure $P + \Delta P$; if (41) is an osmotic equilibrium, then (42) it is also, therefore.

At last we still consider the osmotic equilibrium:

$$G_P \mid L_P \dots \dots \dots (43)$$

We now imagine that fig. 1 (XVII) is valid for this pressure P ; then the vapour G is represented by a point of the gas-branch and the liquid L by a point of the liquid-branch of an isotonic curve; if, therefore, G is represented by a point f.i. of curve hc then L is situated anywhere on curve c_1l_1 .

We now bring the pressure of (43) to $P + \Delta P$ and we take ΔP positive; we then get the osmotic system:

$$G_{P+\Delta P} \rightarrow L_{P+\Delta P} \dots \dots \dots (44)$$

in which both the phases have no more the same *O.W.A.* That of the left system decreases viz. with $\Delta V_G \cdot \Delta P$ and that of the right system with $\Delta V_L \cdot \Delta P$ and as in general we may assume that $\Delta V_G > \Delta V_L$, the right system has a greater *O.W.A.* than the left, therefore. Consequently the water diffuses in (44) in the direction of the arrow. This follows also, when applying the rule, that the water on increase of pressure diffuses in such direction that the total volume decreases.

(To be continued).