Chemistry. — *The osmotic vapour-pressure*, II. By F. A. H. SCHREINE-
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In the osmotic equilibrium:

$$(L) P \mid M(W) \mid (W \ vapour) \, \pi_w \quad . \quad . \quad . \quad . \quad . \quad (1)$$
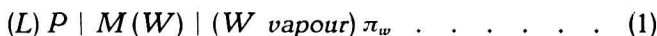
is a liquid L under the pressure P on the left side of the membrane
$M(W)$ and on the right side W-vapour under the pressure π_w. If we
increase the pressure on the right side of membrane a little, then some
W-vapour will condense right through the membrane into the liquid;
if we decrease the pressure a little, then some water will evaporate from
the liquid through the membrane. Consequently π_w is the pressure with
which the liquid L presses the W-vapour through the membrane; for
this reason we have called π_w the *O.W.V.P.* (Osmotic-Water-Vapour-
Pressure) of the liquid L.

Besides the W-vapour of (1) we now also bring the vapours of the
other substances A, B, C etc.; then we get an osmotic equilibrium,
which we shall represent by:

$$(L) P \mid M(W) \mid \left(\frac{aA + bB \ldots + wW}{vapour} \right) \pi \quad . \quad . \quad . \quad (2)$$
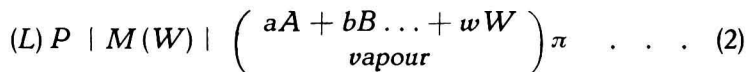
So on the right side of the membrane is a mixture of vapours of the
composition:

$$a \ mol \ A + b \ mol \ B, .. + w \ mol \ W \quad . \quad . \quad . \quad . \quad (3)$$

in which:

$$a + b \ldots + w = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The added substances A, B etc. may be components of the liquid L;
they may also represent strange substances, however, viz. substances,
not occurring in the liquid L. We assume that the gas-laws obtain for
this mixture of vapours.

We imagine the mixture of vapours (3) in a space under a pressure
π; if only the W-vapour were present in this space, the pressure in
this space would not be π, but smaller, viz. $w\pi$; this pressure $w\pi$ is
the partial *V.P.* of the W-vapour in the mixture of vapours.

In system (1) the pressure of the W-vapour on the membrane is π_w;
as the substances A, B etc. of the mixture of vapours in (2) have no
influence on the diffusion of the W-vapour through the membrane, the
pressure of the W-vapour in this mixture of vapours must, therefore,
also be π_w. So we may say:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane, the partial $V.P.$ of the W-vapour of this mixture of vapours will be equal to π_w, viz. equal to the $O.W.V.P.$ of the liquid. Hence follows that between π and π_w the ratio:

$$w\pi = \pi_w \quad \text{or} \quad \pi = \frac{\pi_w}{w} \qquad \ldots \quad \ldots \quad \ldots \quad (5)$$

exists.

We now compare the osmotic equilibria (1) and (2) viz.

$$(L)\, P \mid M\,(W) \mid (W\ vapour)\,\pi_w \qquad \ldots \quad \ldots \quad \ldots \quad (6^a)$$

$$(L)\, P \mid M\,(W) \mid \left(\frac{aA + bB \ldots + wW}{vapour} \right) \pi \qquad \pi = \frac{\pi_w}{w} \qquad (6^b)$$

which both have a membrane $M\,(W)$. Here π_w is the $O.W.V.P.$ of the liquid; consequently π_w has a determined value, only depending on the composition and the pressure of the liquid L.

The pressure π of the mixture of vapours can have an infinite number of values, however; for, as is shown by (6^b), it depends not only upon π_w, but also upon w, viz. upon the W-amount of the mixture of vapours. It appears from (6^b) that π is always greater than π_w, but that it approaches π_w more closely as w increases; when w becomes $= 1$, so that the vapour in (6^b) only consists of W-vapour and (6^b) consequently passes into (6^a), π becomes $= \pi_w$; so we may consider (6^a) also as a special case of (6^b).

It appears from the preceding that in general we may say:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane $M\,(W)$, the pressure π of this mixture will be equal to π_w: w viz. the $O.W.V.P.$ of the liquid, divided by the W-amount of the vapour.

When S is also a volatile substance of the liquid L, then we can with the aid of a membrane $M\,(S)$ get the osmotic equilibria:

$$L\,(P) \mid M\,(S) \mid (S\text{-}vapour)\,\pi_s \qquad \ldots \quad \ldots \quad \ldots \quad (7^a)$$

$$L\,(P) \mid M\,(S) \mid \left(\frac{aA + bB \ldots + sS}{vapour} \right) \pi \qquad \pi = \frac{\pi_s}{s} \quad \ldots \quad (7^b)$$

Consequently π_s here is the $O.S.V.P.$ of the liquid. We now find $\pi = \pi_s : s$. So from this follows for any substance S:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane $M\,(S)$, the pressure π of this mixture is equal to $\pi_s : s$ viz. the $O.S.V.P.$ of the liquid, divided by the S-amount of the vapour.

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We now take a liquid L, containing the volatile substances X, Y, Z, W etc. With the aid of the membranes indicated we then can obtain the osmotic equilibria:

$$(L) P \mid M(X) \mid (X\text{-}vapour) \, \pi_x \quad . \quad . \quad . \quad . \quad . \quad (8^a)$$

$$(L) P \mid M(Y) \mid (Y\text{-}vapour) \, \pi_y \quad . \quad . \quad . \quad . \quad . \quad (8^b)$$

$$(L) P \mid M(Z) \mid (Z\text{-}vapour) \, \pi_z \quad . \quad . \quad . \quad . \quad . \quad (8^c)$$

$$(L) P \mid M(W) \mid (W\text{-}vapour) \, \pi_w \quad . \quad . \quad . \quad . \quad . \quad (8^d)$$

etc. With the aid of a membrane $M(n)$ we then get an osmotic equilibrium:

$$(L) P \mid M(n) \mid \left(\frac{xX + yY + zZ + wW}{vapour} \right) \pi \, . \quad . \quad . \quad . \quad (9)$$

of which the pressure π and the composition of the mixture of vapours have been determined. It follows from the preceding that $\pi_x, \pi_y, \pi_z, \pi_w$, etc. have been determined by the composition and the pressure P of the liquid L.

In (8^a) the pressure of the X-vapour on the membrane is π_x; therefore, in (9) the pressure of the X-vapour in the mixture of vapours must also be π_x; as this pressure is $x\pi$, it follows $x\pi = \pi_x$. If we compare system (9) besides with the systems (8^b), (8^c), (8^d), etc. then we find:

$$x\pi = \pi_x \; ; \quad y\pi = \pi_y \; ; \quad z\pi = \pi_z \; ; \quad w\pi = \pi_w \quad . \quad . \quad . \quad (10)$$

etc. As $x + y + z + w \ldots . 1$, follows:

$$\pi = \pi_x + \pi_y + \pi_z + \pi_w + \ldots . . \quad . \quad . \quad . \quad . \quad (11)$$

so that π has been determined.

It appears from (9) that π is the pressure with which the liquid L presses the $(X + Y + Z + W \ldots .)$ vapour through the membrane; for this reason we call π the $O.(X + Y + Z + W \ldots .) V.P.$ or the total $O.V.P.$ of the liquid. Then it appears from (11):

the total $O.V.P.$ of a liquid is equal to the sum of the $O.V.P.$'s of each of the components.

As π is known now, x, y, z, w etc. follow from (10), so the composition of the mixture of vapours in (9).

We now shall explain the above more in detail. The $O.X.A.$ of a liquid with the composition:

$$x \; mol \; X + y \; mol \; Y + (1 - x - y) \; mol \; W \quad . \quad . \quad . \quad (12)$$

has been determined by (comp. Gen. VI):

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

If we have a liquid of the composition

$$a \; mol \; A + b \; mol \; B + c \; mol \; C + \ldots . \quad . \quad . \quad . \quad (14)$$

in which we take

$$a + b + c + \ldots = 1 \quad \cdots \quad \cdots \quad (15)$$

then the O.A.A., the O.B.A., etc. have been determined by:

$$\left. \begin{array}{l} - \xi_a = \zeta + (1 - a) \dfrac{\partial \zeta}{\partial a} - b \dfrac{\partial \zeta}{\partial b} - c \dfrac{\partial \zeta}{\partial c} \cdots \\[2mm] - \xi_b = \zeta - a \dfrac{\partial \zeta}{\partial a} + (1 - b) \dfrac{\partial \zeta}{\partial b} - c \dfrac{\partial \zeta}{\partial c} \cdots \end{array} \right\} \quad \cdots \quad (16)$$

etc. This also obtains for a vapour of the composition (14); if this obeys the gas-laws, we have:

$$\zeta = a\, Z_a + b Z_b + c Z_c + \ldots + RT\, [a\, log\, a + b\, log\, b + c\, log\, c + \ldots] \quad (17)$$

If we calculate from this $\partial\zeta : \delta a$, $\delta\zeta : \partial b$, etc and if we take (15) into consideration, then we find:

$$\left. \begin{array}{l} - \xi_{a.v} = Z_a + RT\, log\, a \\ - \xi_{b.v} = Z_b + RT\, log\, b \end{array} \right\} \quad \cdots \quad (18)$$
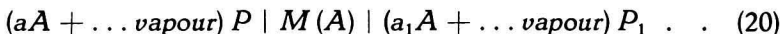
etc. in which the index v indicates that these O.A.'s obtain for a vapour.

In the special case that the vapour consists of a single substance only (e.g. of A, then $a = 1$ or of B, then $b = 1$, etc.) follows from (18):

$$- \xi_{a.v} = Z_a \quad ; \quad - \xi_{b.v} = Z_b \, ; \text{ etc.} \quad \cdots \quad (19)$$

which may be seen at once.

We now begin by considering an osmotic equilibrium:

$$(aA + \ldots \text{vapour})\, P \mid M\, (A) \mid (a_1 A + \ldots \text{vapour})\, P_1 \quad \cdots \quad (20)$$

in which a mixture of vapours containing the substance A is on both sides of the membrane $M\,(A)$; the other substances may be the same as well as different. As the O.A.A. of both the mixtures of vapours must be equal, it follows from (18):

$$(Z_a)_P + RT\, log\, a = (Z_a)_{P_1} + RT\, log\, a_1 \quad \cdots \quad (21)$$

As $\dfrac{\partial Z}{\partial P} = V = \dfrac{RT}{P}$, we find:

$$(Z_a)_P - (Z_a)_{P_1} = \int_{P_1}^{P} \frac{RT}{P}\, dP = RT\, log\, \frac{P}{P_1}. \quad \cdots \quad (22)$$

Now it follows from (21)

$$RT\, log\, P + RT\, log\, a = RT\, log\, P_1 + RT\, log\, a_1 \quad \cdots \quad (23)$$

or:

$$aP = a_1 P_1 \quad \cdots \quad \cdots \quad \cdots \quad (24)$$

So system (20) is in osmotic equilibrium when the pressure of the A-vapour is the same in both mixtures of vapours.

So in the special case that one of the vapour-phases consists of A-vapour only, the pressure of the A-vapour in the mixture of vapours must be equal to the pressure of the A-vapour. So if we have an osmotic-equilibrium

$$(aA + \dot{.} \ldots vapour)\, P \mid M(A) \mid (A\text{-}vapour)\, P_a \quad . \quad . \quad . \quad (25)$$

then it follows

$$aP = P_a$$

Between the pressure π in system (9) and the pressures π_x, π_y etc. in the systems (8) the relations (10) exist; it now follows from the above that the mixture of vapours of system (9) can be in osmotic equilibrium with each of the vapours of the systems (8).

In system (8^a) the $O.X.A.$ of the liquid is equal to the $O.X.A.$ of the vapour; as this consists of X-vapour only,

$$-(\xi_x)_P = (Z_x)_{\pi_x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26^a)$$

will obtain.

For the osmotic equilibria (8^b) etc. follows:

$$-(\xi_y)_P = (Z_y)_{\pi_y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26^b)$$

$$-(\xi_z)_P = (Z_z)_{\pi_z} \quad . \quad . \quad (26^c) \qquad -(\xi_w)_P = (Z_w)_{\pi_w} \quad . \quad . \quad (26^d)$$

etc. The membrane of system (9) is permeable for all substances; the $O.X.A.$, the $O.Y.A.$ etc. of the liquid must consequently be equal to that of the mixture of vapours. So for system (9) obtains:

$$\left. \begin{array}{l} -(\xi_x)_P = (Z_x)_\pi + RT \log x \quad ; \quad -(\xi_y)_P = (Z_y)_\pi + RT \log y \\ -(\xi_z)_P = (Z_z)_\pi + RT \log z \quad ; \quad -(\xi_w)_P = (Z_w)_\pi + RT \log w \end{array} \right\} \quad (27)$$

etc. From (26^a) and the first equation (27) follows:

$$(Z_x)_{\pi_x} = (Z_x)_\pi + RT \log x \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We find from this $\pi_x = x\pi$. In a corresponding way we find also $\pi_y = y\pi$ etc. viz. the relations which have been mentioned already in (10).

If we change the pressure P in system (9), the composition of the liquid remaining constant, it follows from (27):

$$\left. \begin{array}{l} \triangle v_z \,.\, dP = V d\pi + \dfrac{RT}{x}\, dx \quad ; \quad \triangle v_y \,.\, dP = V d\pi + \dfrac{RT}{y}\, dy \\[2mm] \triangle v_z \,.\, dP = V d\pi + \dfrac{RT}{z}\, dz \quad ; \quad \triangle v_w \,.\, dP = V d\pi + \dfrac{RT}{w}\, dw \end{array} \right) \quad (29)$$

etc. If we add these up, after having multiplied the first by x, the second by y, etc., bearing in mind that $x + y + \ldots = 1$, it follows:

$$d\pi = \frac{\triangle v_t}{V_\pi}\, dP \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

V_π is the volume of 1 grammol. of vapour under the pressure π and

$$\triangle v_t = x \triangle v_x + y \triangle v_y + z \triangle v_z + w \triangle v_w .$$

So $\triangle v_t \, dn$ is the increase of volume of the liquid, when this absorbs xdn quant. of X, ydn quant. of Y, etc. So, as $\triangle v_t$ is generally positive, it follows from (30):

if we increase the pressure P of a liquid, then π, viz. its total $O.V.P.$ will increase.

This change in pressure is accompanied by a change dx, dy etc. of the mixture of vapours, which we can calculate from (29); a detailed consideration is left to the reader.

In the osmotic equilibrium

$$(L) \, P \mid M \, (W) \mid (W\text{-}vapour) \, \pi_w \quad . \quad . \quad . \quad . \quad (31)$$

π_w has been determined by the composition and the pressure P of the liquid L. In paper I we have found the equation (19) for it; if we here give the index w to π and $\triangle v$, we get:

$$log \, \pi_w = log \, P_0 + \frac{P - P_0}{RT} \triangle v_w \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Here P_0 is the vapourpressure of the liquid L, therefore, the pressure under which te equilibrium:

$$(L + W\text{-}vapour) \, P_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

can exist, without the necessity of putting a membrane between both phases.

This shows it has been assumed that only one of the substances of L is volatile; if the liquid contains other volatile substances besides, e.g. X, Y, Z, W etc. then under the pressure P_0 we have the equlibrium:

$$[L + (x_0 \, X + y_0 \, Y + z_0 \, Z + w_0 \, W \ldots) \, vapour] \, P_0 \quad . \quad . \quad (34)$$
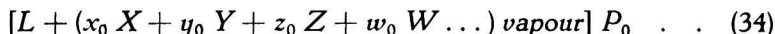
in which x_0, y_0 etc. represent the composition of this mixture of vapours. We now must introduce a small change in (32) also; for this we follow the same way as in paper I.

As (31) is the same as (8^d), (26^d) obtains here; from this it follows (comp. Paper I):

$$\triangle v_w . dP = V d\pi_w = RT \frac{d\pi_w}{\pi_w} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

From this it follows:

$$\triangle v_w . P = RT \, log \, \pi_w + C \quad . \quad . \quad . \quad . \quad . \quad (36)$$

In order to determine the contstant C, we now take the liquid L under its own vapourpressure P_0. If the vapour only contains W-vapour, we

consequently have the equilibrium (33). If a membrane $M(W)$ is put into it, we get the osmotic equilibrium;

$$(L) P_0 \mid M(W) \mid (W\text{-}vapour) P_0 \quad . \quad . \quad . \quad . \quad . \quad (37)$$

in which the pressure is the same on both sides of the membrane.

So we also can satisfy (36) by $P = P_0$ and $\pi_w = P_0$; we then get:

$$\triangle v_w . P_0 = RT \, log \, P_0 + C \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Now (32) follows from (36) and (38).

When, however, the liquid L contains more volatile substances, then we have the equilibrium (34) under the pressure P_0; if a membrane $M(n)$ is put in, we get:

$$(L) P_0 \mid M(n) \mid \left(\frac{x_0 \, X + y_0 \, Y + z_0 \, Z + w_0 \, W \ldots}{vapour} \right) P_0. \quad . \quad (39)$$

As the pressure of the W-vapour in the mixture of vapours is $w_0 P_0$, in the system

$$(L) P_0 \mid M(W) \mid (X\text{-}vapour) \, w_0 P_0 \quad . \quad . \quad . \quad . \quad (40)$$

the pressure on the right side of the membrane must be $w_0 P_0$. So we now can satisfy (36) by $P = P_0$ and $\pi_w = w_0 P_0$; instead of (38) we then get:

$$\triangle v_w . P_0 = RT \, log \, w_0 P_0 + C \quad . \quad . \quad . \quad . \quad . \quad (41)$$

From (36) and (41) now follows:

$$log \, \pi_w = log \, w_0 P_0 + \frac{P_0 - P}{RT} \triangle v_w \quad . \quad . \quad . \quad . \quad (42^a)$$

or:

$$log \, \pi_w = log \, P_0 + \frac{P_0 - P}{RT} \triangle v_w + log \, w_0 \quad . \quad . \quad . \quad (42^b)$$

If, therefore, we have a liquid of which more substances are volatile, then its $O.W.V.P.$ is no longer determined by (32), but by (42^a) or (42^b).

We may consider (32) as a special case of (42^a) or (42^b); when namely the vapour consists of W only, then $w_0 = 1$ and (42^a) and (42^b) pass into (32).

For an osmotic system

$$(L) P \mid M(W) \mid (L') P' \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

we found in paper I the equation (22); if in this we give to π and π' the index w, we have, therefore:

$$(\xi_w)_P - (\xi'_w)_{P'} = RT \, log \, \frac{\pi'_w}{\pi_w} \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Here ξ_w and ξ'_w are the $O.W.A.$, π_w and π'_w the $O.W.V.P.$ of the liquids L and L'.

As the direction in which the water diffuses through the membrane

depends upon the sign of the first part of (44) and, therefore, also upon that of the second part, it follows from this (comp. also Paper I):
the water diffuses through a membrane $M(W)$ towards that side, where the *O.W.V.P.* is smallest.

If we substitute the membrane $M(W)$ by a membrane $M(X)$, we have the system:

$$(L)\,P \mid M(X) \mid (L')\,P' \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

For this obtains:

$$(\xi_x)_P - (\xi'_x)_{P'} = RT\,log\,\frac{\pi'_x}{\pi_x} \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Consequently for the direction of the diffusion of the substance X the same obtains as above for the substance W. So we may say in general:
a substance S diffusses through a membrane $M(S)$ towards that side, where the *O.S.V.P.* is smallest.

We now take the osmotic system:

$$(L)\,P \mid M(n) \mid (L')\,P'$$
$$\longleftarrow \alpha X \quad ; \quad \longleftarrow \beta Y \quad ; \quad \longleftarrow \gamma Z \quad ; \quad \longleftarrow \delta W \Big\} \quad . \quad (47)$$

in which a membrane $M(n)$, so that all substances diffuse. We assume that α quant. of X, β quant. of Y etc. diffuse towards the left (when one of these quantities is negative, then the corresponding substance diffuses towards the right). As we have seen in Gen. VI, now α, β, γ etc. have to satisfy:

$$\alpha K_x + \beta K_y + \gamma K_z + \delta K_w \ldots > 0 \quad . \quad . \quad . \quad . \quad (48)$$

The direction in which a substance runs through the membrane $M(n)$ is, therefore, no longer determined by the *O.A.* of that substance only, but by the *O.A.*'s of all substances together and by the nature of the membrane.

We now may also give an other form to (48). If we represent the *O.X.V.P.* the *O.Y.V.P.*, etc. of the liquid L by π_x, π_y etc. and those of the liquid L' by π'_x, π'_y etc., we have:

$$K_x = RT\,log\,\frac{\pi'_x}{\pi_x} \quad ; \quad K_y = RT\,log\,\frac{\pi'_y}{\pi_y} \; ; \; \text{etc.} \quad . \quad . \quad . \quad (49)$$

Substituting these values in (48), we find that α, β, γ etc. have to satisfy:

$$\left(\frac{\pi'_x}{\pi_x}\right)^\alpha \left(\frac{\pi'_y}{\pi_y}\right)^\beta \left(\frac{\pi'_z}{\pi_z}\right)^\gamma \left(\frac{\pi'_w}{\pi_w}\right)^\delta \ldots > 1 \quad . \quad . \quad . \quad (50)$$

From this it follows among other things:
a substance X can diffuse through a membrane $M(n)$ from greater towards smaller-as well as from smaller towards greater *O.X.V.P.*

Of course the same obtains for the other substances.

Previously we have said:

a substance S passes congruently through a membrane, when it diffuses in the same direction as through a membrane $M(S)$; it diffuses incongruently when it runs through the membrane in opposite direction.

From this followed:

a substance S runs congruently through a membrane, when it diffuses from smaller towards greater- and incongruently when it diffuses from greater towards smaller $O.S.A.$

So now we may say also:

a substance S runs congruently through a membrane, when it diffuses from greater towards smaller- and incongruently when it diffuses from smaller towards greater $O.S.V.P.$

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