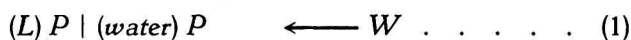


Chemistry. — *The osmotic vapour-pressure*, I. By F. A. H. SCHREINER-MAKERS.

(Communicated at the meeting of March 23, 1929).

In the osmotic system



we find on the left side of the membrane a liquid L and on the right side pure water; on both sides the pressure is P (we imagine e. g. $P = 1$ atmosphere). When this membrane is permeable for water only, the water will diffuse in the direction of the arrow, viz. towards the left.

We now increase the pressure of the liquid L till no more W can diffuse, keeping the temperature constant; then (1) passes into the osmotic equilibrium:



The difference in pressure $P_1 - P$ is the *O. P.* (Osmotic Pressure); in order to distinguish this from another *O. P.*, which we shall discuss later on, we shall call $P_1 - P$ the increase of *O. P.*

With this increase of pressure the liquid L can remain stable; it can also become metastable, however, or even labil. If e. g. it deposits the solid substance F , then instead of (1^a) arises the osmotic equilibrium



in which of course L_1 has an other composition than L ; consequently the pressure P_2 and, therefore, also the increase of *O. P.* differs in (1^b) from that in (1^a).

We can also imagine that L when pressure is increased should de-mix into two liquids; we then get:



with an other increase of *O. P.* than in (1^a) and (1^b).

We can also prevent the diffusion of the water in (1) by lowering the pressure on the right side of the membrane; we then get:



When the pressure π is greater than the vapour-tension of the water, this will remain fluid; if, however, π is smaller, we get water-vapour. So it depends on the pressure π whether the water on the right side of the membrane will be present either as a liquid or as vapour; this has been indicated in (1^d) by the letters l and v . Now we shall call the difference in pressure $P - \pi$ the decrease of *O. P.*

If we now compare the decrease of *O. P.* with the increase of *O. P.* in system (1), it appears:

the *O. P.*-decrease depends only on the properties the liquid *L* has under the pressure *P*;

the *O. P.*-increase, however, depends on the properties this liquid gets, when pressure is increased; in this case it may or may not deposit a solid substance or de-mix into two liquids, etc.

In the osmotic system



is a liquid saturated with solid *F* on the left side of the membrane. We now increase the pressure on the left side of the membrane till an osmotic equilibrium is reached. When the solubility of *F* increases with increase of pressure, we may distinguish two cases.

a. From (2) arises the osmotic equilibrium



in which *L*₁ has another composition than *L*.

b. The solid substance *F* disappears entirely with the increase of *P*; then we get the osmotic equilibrium:



in which *L*₂ has an other composition than *L* or *L*₁. This system (2^b) will occur when too little solid *F* is present in (2) or when by the increase of *P* the melting-point of *F* is lowered even below the temperature of the system.

We now imagine in (2) *n* quant. of *L* and *m* quant. of *F*; the composition of *L*₁ and the *O. P.*-increase *P*₁—*P* then are independent of *n*:*m* and, therefore, completely determined. The composition of *L*₂, however, does depend of *n*:*m*; so the *O. P.*-increase *P*₂—*P* will change with *n*:*m* and consequently can have an infinite number of values.

We now lower the pressure on the right side of the membrane in (2) till no more *W* diffuses; we then get the osmotic equilibrium:



with the *O. P.*-decrease *P*—*π*. The system *L* + *F* is still present here unchanged, whereas in (2^a) and (2^b) it has passed into an other. From this it appears:

the *O. P.*-decrease only depends on the properties the phases *L* and *F* have under the pressure *P*; this *O. P.*-decrease is independent of *n*:*m* and completely determined.

the *O. P.*-increase, however, depends on the phases, formed under increase of pressure; this *O. P.*-increase is dependent on *n*:*m* and can have an infinite number of values.

Corresponding considerations obtain also when we put some arbitrary

system or other e.g. $L + F + F'$ or $L + L'$, etc. on the left side of the membrane. So, if we wish to deduce a property of a liquid or of a system with the aid of the *O. P.*, the *O. P.*-decrease is more useful in this respect than the *O. P.*-increase, which not only changes the system, but can also have an infinite number of values. For this reason we shall in our next considerations use the *O. P.*-decrease or a pressure, connected with it.

At first we take an equilibrium

$$(L + W \text{ vapour}) P_0 \dots \dots \dots (3)$$

in which there is no membrane between the liquid and the *W*-vapour. If we keep the temperature and the composition of the liquid constant, this system will exist only under a definite pressure P_0 ; this is the *W. V. P.* (*Water-Vapour-Pressure*) of the liquid. We now imagine this system under a piston; if we slightly increase the pressure on this piston, so that it becomes a little higher than P_0 , some *W*-vapour will condense; if we slightly decrease this pressure, some water evaporates.

We have something like this in the osmotic equilibrium:

$$(L) P \left| \begin{array}{c|c} a & d \\ \hline W \text{ vapour} & \pi \\ \hline b & c \end{array} \right. \dots \dots \dots (4)$$

in which ab is a membrane, permeable for water only. On its left side is a liquid under the pressure P and on its right side a space $abcd$ in which *W*-vapour under the pressure π .

We now imagine that cd is a movable piston; if we slightly increase the pressure on this piston, *W*-vapour will pass through the membrane towards the liquid; we may say that *W*-vapour condenses in L through the membrane. If we decrease the pressure on the piston a little, water will evaporate through the membrane. So we have a "condensation" and "evaporation" of water through a membrane; for this reason we shall call π : the vapour-tension of the liquid through the membrane or the *O. W. V. P.* (*Osmotic-Water-Vapour-Pressure*) of the liquid.

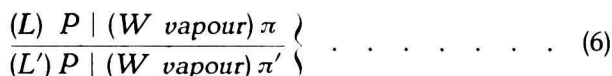
In system (3) liquid and vapour can only exist under a definite pressure P_0 , in (4), however, the liquid can exist under an infinite number of pressures P and with every pressure P goes a definite pressure π of the vapour. So we may say:

the *W. V. P.* of a liquid has a definite value P_0 ; the *O. W. V. P.*, however, has an infinite number of values π ; we shall see that $\pi > P_0$.

We now take the osmotic equilibria

$$\left. \begin{array}{l} (L) P \mid (W \text{ vapour}) \pi \\ (L') P \mid (W \text{ vapour}) \pi' \end{array} \right\} \dots \dots \dots (5)$$

In the first the liquid L has an $O.W.V.P. = \pi$ and in the second the liquid L' an $O.W.V.P. = \pi'$. When L and L' are different, π and π' will generally be different too; when, however, L and L' have the same $O.W.A.$, then $\pi = \pi'$. In order to prove the last statement we form the new osmotic system:



in which also the horizontal dash represents a membrane $M(W)$. Now we imagine each of the two vapour-phases in a closed space. If $\pi > \pi'$, then W -vapour would diffuse from the higher towards the lower vapour-space; as the pressure in the higher space will consequently decrease, water will evaporate from L towards the right; as, however, the pressure increases in the lower vapour-space, W -vapour will condense in L' . As, therefore, the $O.W.A.$ of L increases and that of L' decreases, water will now also diffuse from L' towards L .

If we now regulate the surface of the membranes in such a way that the same quantity of water runs through all membranes in the same time, then neither the compositions of the liquids nor the pressures π and π' will change; we then get an eternal circular current of water and water-vapour.

When $\pi < \pi'$, this circular current would run in the opposite direction.

As we assume that these circular currents are not possible, it follows $\pi = \pi'$; so we find:

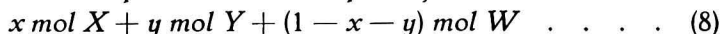
all liquids with the same $O.W.A.$ have also the same $O.W.V.P.$ (consequently they have also the same $O.P.$ -decrease; their $O.P.$ -increase will generally be different).

As all liquids of the isotonic W -curve ab (fig. 1 Gen. VI) have the same $O.W.A.$, they consequently will have the same $O.W.V.P.$ too; the same obtains for the liquids of the curve $a_1 b_1$ and for those of $a_2 b_2$. As we shall see further on, however, the liquids of $a_1 b_1$ have a greater $O.W.V.P.$ than those of ab and these again a greater $O.W.V.P.$ than those of $a_2 b_2$.

Now we consider the osmotic equilibrium:



We represent the composition of the liquid by



we shall call the thermodynamical potential of one quantity of liquid and vapour ζ and Z .

Now we imagine that dn quantities of vapour condense through the membrane in the liquid; we now find (comp. e. g. Gen. VI) that (7) is an osmotic equilibrium, when

$$\left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \right)_p = Z_\pi \dots \dots \dots (9)$$

has been satisfied. The *O.W.A.* of a liquid viz. ξ_w is, as we have seen in Gen. VI, determined by:

$$\xi_w = -\zeta + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \dots \dots \dots (10)$$

Consequently we may write instead of (9):

$$-(\xi_w)_P = Z_\pi \dots \dots \dots (11)$$

So the *O.W.V.P.* of the liquid, namely π is determined by its *O.W.A.* From this follows, what we have already found above in an other way: all liquids with the same *O.W.A.* also have the same *O.W.V.P.* From (11) follows:

$$-d(\xi_w) = V d\pi \dots \dots \dots (12)$$

this means: the *O.W.V.P.* of a liquid decreases (increases) when its *O.W.A.* increases (decreases).

This is indeed clear; the water of the liquid in (7) namely tries to diffuse through the membrane towards the outside; it is prevented to do this however, by the *O.W.A.* of the liquid itself and by the pressure π of the vapour. So the greater one influence is, the smaller may be the other.

From the above follows among other things:

all liquids of an isotonic *W*-curve have the same *O.W.V.P.*; this will be greater, the closer this curve is situated to point *W* (fig. 1 Gen. VI).

Previously we have seen among other things:

the water diffuses through a membrane *M(W)* towards that side, where the *O.W.A.* is greatest.

Therefore, we may also say now:

the water diffuses through a membrane *M(W)* towards that side where the *O.W.V.P.* is smallest.

If we keep the composition of the liquid in (7) constant, and change the pressure, it follows from (9) or (11):

$$d\pi = \frac{\Delta v}{V} dP \dots \dots \dots (13)$$

in which, as follows from (9) or (11):

$$\Delta v = v - x \frac{\partial v}{\partial x} - y \frac{\partial v}{\partial y} \dots \dots \dots (14)$$

We see from this that $\Delta v \cdot dn$ is the increase of the volume of the liquid, when this absorbs dn quantities of water; this increase of volume is generally positive. *V* is the volume of the *W*-vapour under the pressure π . From (13) now follows:

with increase of pressure the *O.W.V.P.* of a liquid increases.

In general, however, $d\pi$ is small with respect to dP ; the volume *V*

of a grammolecule W -vapour under a low pressure π is namely ten thousand times larger than the volume v of a grammolecule water and, therefore, also larger than Δv . From this appears:

In general the *O.W.V.P.* of a liquid will increase only a little when the pressure P is raised.

So the osmotic equilibrium (7) is comparatively insensible to a small change in the pressure of the liquid, but very sensible to a small change in the pressure of the vapour.

As a special case of (7) the pressure can also be the same on both sides of the membrane. In system (3) namely the liquid under a pressure P_0 is in equilibrium with vapour under the same pressure P_0 ; of course this still remains so when we put a membrane $M(W)$ between liquid and vapour. We then get:

$$(L) P_0 \mid (W \text{ vapour}) P_0 \dots \dots \dots (15)$$

in which P_0 is the *W.V.P.* of the liquid. Therefore, the *O.W.V.P.* of the liquid is now equal to its *W.V.P.* In connection with what we have seen above, it appears from this, that the *O.W.V.P.* of a liquid under a not too high pressure P , will be only very little larger than its *W.V.P.*

If the gas-laws obtain for the vapour, we have $\pi V = RT$; then we may write for (13):

$$RT \frac{d\pi}{\pi} = \Delta v \cdot dP \dots \dots \dots (16)$$

Of course the change in volume Δv is dependent on the pressure P ; between wide limits of P , however, we may look upon Δv as constant. Then follows from (16):

$$RT \log \pi = P \cdot \Delta v + C \dots \dots \dots (17)$$

in which C is a constant. As, however, (17) also obtains for system (15) in which $P = P_0$ and $\pi = P_0$, we consequently also have

$$RT \log P_0 = P_0 \Delta v + C \dots \dots \dots (18)$$

so that C has been determined. We now find:

$$\log \pi = \log P_0 + (P - P_0) \frac{\Delta v}{RT} \dots \dots \dots (19)$$

So if in a diagram we draw $\log \pi$ and P as variables, we will get a straight line.

We now take the two osmotic equilibria:

$$(L) P \mid (W \text{ vapour}) \pi \quad ; \quad (L') P' \mid (W \text{ vapour}) \pi' \dots \dots (20)$$

For them obtain the equations:

$$-(\xi_w)_P = Z_\pi \quad \quad -(\xi')_{P'} = Z_{\pi'} \dots \dots \dots (21)$$

As $Z_{\pi'} - Z_{\pi} = RT \log \frac{\pi'}{\pi}$ it follows:

$$(\xi_w)_P - (\xi_w)_{P'} = RT \log \frac{\pi'}{\pi} \dots \dots \dots (22)$$

consequently a relation between the *O.W.A.* and the *O.W.V.P.* of two different liquids (*L* and *L'*) under two different pressures (*P* and *P'*).

If we take e.g. the osmotic system

$$(L) P \mid (L') P' \dots \dots \dots (23)$$

then the first part of (22) represents the difference of the *O.W.A.* of the two liquids; therefore, the first part will determine the direction in which in (23) the water will diffuse through a membrane *M(W)*; therefore, this direction is determined also by the second part of (22), which contains the *O.W.V.P.* of the two liquids. Instead of:

no water diffuses through a membrane *M(W)* when the two liquids have the same *O.W.A.*;

the water diffuses towards that side of a membrane *M(W)* where the *O.W.A.* is greatest;

we may also say now, therefore:

no water diffuses through a membrane *M(W)* when the two liquids have the same *O.W.V.P.*

the water diffuses towards that side of a membrane *M(W)* where the *O.W.V.P.* is smallest.

We now imagine the second system in (20) replaced by system (15). Then in (22) we have to put $P' = P_0$ and $\pi' = P_0$. When both liquids now have the same compositions, we can replace the first part of (22) by $(P_0 - P) \Delta v$. We then get:

$$(P_0 - P) \Delta v = RT \log \frac{P_0}{\pi} \dots \dots \dots (24)$$

which is in accordance with (19).

In order to give an other form to (9) we put:

$$\zeta = \varphi + RT [x \log x + y \log y + (1 - x - y) \log (1 - x - y)] \dots (25)$$

If we now calculate $\partial \zeta : \partial x$ and $\partial \zeta : \partial y$, we see that we may write for (9):

$$\left(\varphi - x \frac{\partial \varphi}{\partial x} - y \frac{\partial \varphi}{\partial y} \right)_P + RT \log (1 - x - y) = Z_{\pi} \dots (26)$$

When the quantities *x* and *y* of the substances *X* and *Y* become nought, the osmotic equilibrium (7) will pass into:

$$(water) P \mid (W \text{ vapour}) P_s \dots \dots \dots (27)$$

in which on the left side of the membrane is pure water. Consequently

P_s is the *O.W.V.P.* of pure water under the pressure P . For this system obtains, as follows from (26):

$$(\varphi_0)_P = Z_{P_s} \dots \dots \dots (28)$$

The index o indicates that x and y are nought; therefore, φ_0 is the thermodynamical potential of pure water. From (26) and (28) now follows:

$$\left(\varphi - x \frac{\partial \varphi}{\partial x} - y \frac{\partial \varphi}{\partial y} - \varphi_0 \right)_P + RT \log (1 - x - y) = Z_\pi - Z_{P_s} \dots (29)$$

If we now take a much diluted liquid, so that x and y are very small, the term with the index P will only consist of magnitudes of the second and higher orders, which may be neglected; now (29) passes into:

$$RT \log (1 - x - y) = RT \log \frac{\pi}{P_s} \dots \dots \dots (30)$$

From this follows:

$$P_s - \pi = (x + y) P_s \dots \dots \dots (31)$$

in which the first part represents the decrease of the *O.W.V.P.*; from this appears:

the *O.W.V.P.* of the water (viz. P_s) is lowered by the addition of other substances; at a first approximation this decrease is proportionate to the added quantities $x + y$ of the new substances.

With the aid of the *O.P.*-increase we can deduce several properties; of course we may also do this by the help of the *O.W.V.P.* or the *O.P.*-decrease, consequent upon this. We shall not do so, however; we namely can find all these properties easily and accurately with the aid of the thermodynamical potential¹⁾, so that a deduction with the aid of the *O.P.*-increase or -decrease themselves, following first from thermodynamical considerations, is an unnecessary round about way. We shall use this *O.W.V.P.* however, which is bound up with the *O.W.A.*, when in subsequent communications we shall consider the diffusion through membranes more in detail.

(To be continued).

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¹⁾ For the first thermodynamical deduction of the exact formula of the *O.P.*-increase, its meaning (diffusion-counter-pressure), etc. comp.

J. J. VAN LAAR:

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