

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

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We take a liquid L of the composition:

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

and a liquid L_0 , which only contains the simple substance W (f.i. water). We imagine both liquids, separated from one another by a semipermeable membrane, which allows to pass freely the substance W only. We call W the diffusing substance, $X Y Z \dots$ the not-diffusing substances. Further we assume that L and L_0 have the same temperature, but that L is under an external pressure P and L_0 under an external pressure P_0 . The osmotic pressure π of the liquid L with respect to L_0 is then $\pi = P - P_0$.

When we allow δn quantities of the diffusing substance W to be transported from the liquid L_0 towards the liquid L , then we find the equation for equilibrium:

$$\left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots \right)_P = (\zeta_0)_{P_0} \quad (2)$$

in which ζ and ζ_0 represent the thermodynamical potentials of the unity of quantity of the liquids L and L_0 . Consequently ζ is a function of P, x, y, \dots and ζ_0 a function of P_0 .

When L is a binary liquid, which contains besides the diffusing substance W still only the substance X , then (2) passes into:

$$\left(\zeta - x \frac{\partial \zeta}{\partial x} \right)_P = (\zeta_0)_{P_0} \quad (3)$$

When we change x, P and P_0 , then follows:

$$-x r . dx + \left(v - x \frac{\partial v}{\partial x} \right) dP = v_0 dP_0 \quad (4)$$

When we keep constant the external pressure P_0 of the liquid L_0 , then $dP_0 = 0$ and $dP = d\pi$; then it follows from (4):

$$d\pi = \frac{x r}{v - x \frac{\partial v}{\partial x}} dx \quad (5)$$

Hereby is defined the relation between the change dx of the concentration of the not-diffusing substance and the change $d\pi$ of the osmotic pressure. In (5) is:

$$r = \frac{\partial^2 \zeta}{\partial x^2} = \frac{RT}{x(1-x)} + \alpha \dots \dots \dots (6)$$

in which α has a finite value. For very small values of x , as $x \frac{\partial v}{\partial x}$ approaches then to zero, (5) passes into:

$$d\pi = \frac{RT}{v} \cdot dx \quad \text{or} \quad \pi = \frac{RT}{v} \cdot x \dots \dots \dots (7)$$

the well-known law of VAN 'T HOFF. When the concentration x of the not-diffusing substance becomes larger, then deviations of this law may occur; (5) remains valid, however.

When x , viz. the concentration of the not-diffusing substance X approaches to 1, then, as is apparent from (6) the numerator of (5) becomes very large. A small change of the concentration shall cause, therefore a very large change of the osmotic pressure.

We now distinguish two principal cases.

I. All liquids under consideration rest homogeneous; consequently no dimixtion into two liquids occurs.

As r is, therefore, always positive, the numerator of (5) is, therefore, also always positive.

In order to find the meaning of the denominator, we mix dn quantities W with one quantity L ; the total new volume v' becomes then:

$$v' = v + \left(v - x \frac{\partial v}{\partial x} \right) dn \dots \dots \dots (8)$$

In general shall be $v' > v$, unless with the mixing a contraction of volume occurs which is still larger than the volume of the added quantity of W . In general the denominator is positive, therefore; this is surely the case for small values of x , as $v - x \frac{\partial v}{\partial x}$ only differs little then from v . As:

$$d \left(v - x \frac{\partial v}{\partial x} \right) = -x \frac{\partial^2 v}{\partial x^2} \cdot dx \dots \dots \dots (9)$$

it appears that the denominator may become negative only then, when the v, x -curve turns its convex side towards the concentration-axis. We now distinguish two cases.

a. The denominator of (5) is always positive.

From (5) follows: with increasing concentration of the not-diffusing substance, the osmotic pressure grows.

We draw in fig. 1 on the horizontal line WX the concentrations

and on the vertical axis the pressures $P = P_0 + \pi$ of the osmotic equilibrium $L + W$. When we take $W a_0 = P_0$, then we get the osmotic pressure-curve $a_0 b c d$. Consequently in a_0 the osmotic pressure is zero; in b, c , etc., it is represented by the length of the perpendiculars fallen on the line $a_0 a'_0$.

The direction of this curve in its beginning-point a_0 is defined by (7)

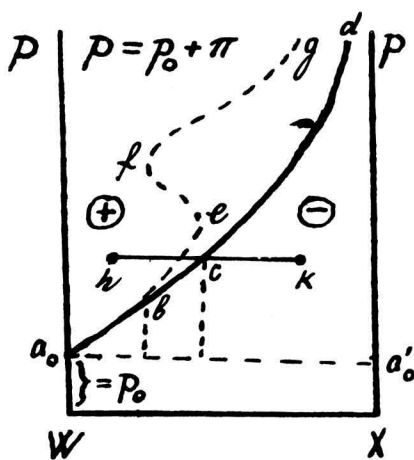


Fig. 1.

viz. the law of VAN 'T HOFF; in the vicinity of the line XP , it shows a straight ascension. The osmotic pressure-curve $a_0 b c d$ divides the diagram into two fields, which we shall call the (+) field and the (-) field; the first one is indicated in the figure by an encircled +, the second one by an encircled -.

An arbitrary point h in the (+) field represents a liquid, which, under the pressure P_h , is not in osmotic equilibrium with the diffusing substance W , but contains too much

of this substance. When we keep the pressure constant, then it passes, depositing the substance W in the liquid c , which is in osmotic equilibrium under this pressure.

A point K in the (-) field represents a liquid, which contains too little of the substance W . Consequently it passes dissolving the diffusing substance W into the liquid c also.

We are able to deduce the osmotic pressure-curve also by other considerations.

We imagine viz. the diffusing substance W to be substituted by an imaginary state of this substance, which we shall call (W) . We define this imaginary state in such a way that the thermodynamical potential of (W) under all pressures is equal to $(\zeta_0)_{P_0}$ viz. to that of the diffusing substance W under the pressure P_0 .

When in (2) $xy \dots$ approach to zero, then the first part becomes equal to the thermodynamical potential of the substance W under the pressure P ; when we call this $(\zeta_W)_P$ then we have:

$$(\zeta_W)_P = (\zeta_0)_{P_0} + \int_{P_0}^P v dP \dots \dots \dots (10)$$

When we take $P > P_0$ then is, therefore $(\zeta_W)_P > (\zeta_0)_{P_0}$; when $P < P_0$ then is $(\zeta_W)_P < (\zeta_0)_{P_0}$.

Instead of the osmotic equilibrium $L + W$ we now take the equilibrium $L + (W)$: as L represents herein the liquids, which are saturated with the imaginary substance (W) we shall call this the "saturation-equilibrium".

For this saturation-equilibrium we find the condition for equilibrium

$$\left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots \right)_P = (\zeta_0)_{P_0} \dots \dots \dots (11)$$

consequently the same as (2). Hence it follows, therefore:

we can replace an osmotic equilibrium $L + W$ with the osmotic pressure $\pi = P - P_0$ by the saturation-equilibrium $L + (W)$ under the pressure $P = P_0 + \pi$.

When a liquid L has an osmotic pressure $\pi = P - P_0$ then this liquid is in equilibrium under the pressure $P = P_0 + \pi$ with the imaginary substance (W); and reversally.

The osmotic pressure-curve $a_0 b c d$ of fig. 1 represents, therefore, also the liquids, which are saturated under the different pressures P with the substance (W); points in the (+) field represent super-saturated solutions, points in the (-) field unsaturated solutions.

Reversally we can also find this osmotic pressure-curve, when we deduce the saturation-curve of the substance (W) under variable pressure.

b. When we assume that the denominator of (5) may become also negative, then the osmotic pressure-curve may have a form as f.i.: the curve $a_0 b e f g$ (fig. 1); on part $f e$ then the osmotic pressure decreases at increasing concentration of the not-diffusing substance. Then there are liquids which have three different osmotic pressures.

When we consider, instead of the osmotic equilibrium $L + W$ the saturation-equilibrium $L + (W)$, then along curve $a_0 b e f g$ with increase of pressure the solubility of the substance (W) decreases firstly as far as e , further it increases as far as f and afterwards it decreases again.

II. Now we shall assume that there are also liquids L , which are dimixed into two other liquids.

When we wish to deduce the shape of the osmotic curve also now with the aid of (5) and other relations, then we have to take into consideration that v can also become negative.

However, we shall replace now the osmotic equilibrium $L + W$ by the saturation-equilibrium $L + (W)$. Consequently we have only to seek for the saturation-curve of the substance (W) when liquids occur, which are dimixed.

Although those saturation-curves are known, yet we will for a moment indicate the way to deduce them graphically.

For this reason we draw on the horizontal axis (fig. 2) the concentrations and on the vertical axis the thermodynamical potentials

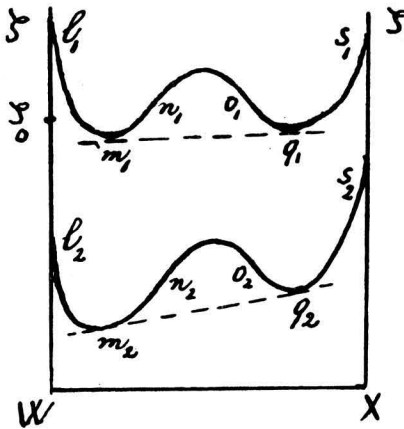


Fig. 2.

of the liquids. We represent $(\zeta_0)_{P_0}$ viz. the thermodynamical potential of the imaginary substance (W) by point ζ_0 . Under a pressure $P_1 > P_0$ the ζ -curve has a form like $l_1 m_1 n_1 o_1 q_1 s_1$; the point l_1 is situated, as formerly is deduced from (10), above the point ζ_0 . As we assume that dimixion may occur, in this ζ -curve two points of inflexion n_1 and o_1 occur. We can, therefore, also draw a double-tangent with the two points of contact m_1 and q_1 . Liquids, represented by points of $l_1 m_1$ and $q_1 s_1$ rest, therefore, homogeneous; the other liquids are dimixed in a complex of the two liquids m_1 and q_1 . The liquids, situated between m_1 and n_1 and those between o_1 and q_1 are metastable, the liquids between n_1 and o_1 are unstable ones.

We now imagine the tangents to be drawn in the points of inflexion n_1 and o_1 ; their points of intersection with the axis $W\zeta$ are called n'_1 and o'_1 . We now may distinguish several cases.

1. The point ζ_0 is situated below the point of intersection n'_1 . Only one tangent to the ζ -curve can be drawn from ζ_0 ; consequently under the pressure P_1 there is only one liquid, which is saturated with the substance (W); consequently also: there is only one liquid with the osmotic pressure $\pi = P_1 - P_0$. This liquid is stable and is situated between q_1 and s_1 .

2. The point ζ_0 is situated between n'_1 and o'_1 .

Now we can draw from ζ_0 three tangents to the ζ -curve; consequently there are three liquids with the same osmotic pressure $\pi = P_1 - P_0$; one of these liquids is stable, one metastable and one unstable. When the point ζ_0 is situated above the double-tangent $m_1 q_1$ then the stable liquid is situated between l_1 and m_1 ; when ζ_0 is situated below the double-tangent, then the stable liquid is situated between q_1 and s_1 .

When accidentally the point ζ_0 is situated on the double-tangent then there are two stable liquids viz. m_1 and q_1 , which have the same osmotic pressure; the third one is unstable.

3. The point ζ_0 is situated above the point o'_1 :

As ζ_0 is situated below l_1 , ζ_0 is situated, therefore, between o'_1 and l_1 . Only one tangent can be drawn from ζ_0 now; consequently there is only one solution saturated with the substance (W), consequently also only one liquid with the osmotic pressure $\pi = P_1 - P_0$. This liquid is stable and is situated between l_1 and m_1 .

On decrease of pressure all points of the ζ curve shift downwards; its form changes therewith at the same time. Under a pressure $P = P_0$ it goes through the point ζ_0 , which rests on its place at change of pressure; under a pressure $P_2 < P_0$ it may be represented f.i. by curve $l_2 m_2 n_2 o_2 q_2$. As $\pi = P_2 - P_0$ is negative now, the osmotic pressure is negative, therefore. We now may distinguish two cases.

4. The point ζ_0 is situated above the point of intersection o'_2 .

Consequently no tangent can be drawn from ζ_0 to the ζ curve; consequently there is also no liquid with the considered negative osmotic pressure.

5. The point ζ_0 is situated below the point of intersection o'_2 .

Consequently from ζ_0 two tangents can be drawn to the ζ curve; therefore there are under the pressure P_2 two liquids, both saturated with the substance (W), consequently also two liquids with the negative osmotic pressure $\pi = P_2 - P_0$. One of these liquids is metastable, the other one is unstable.

Firstly we imagine a very low pressure, so that the ζ curve is situated far below the point ζ_0 ; on increase of P it then shifts upwards, under a pressure $P = P_0$ it goes through the point ζ_0 and on further increase of pressure it comes above the point ζ_0 . As the ζ curve changes also its form with this change of pressure, there may be also pressures, under which its concave part is disappearing, so that it gets downwardly totally a convex shape. When we consider at each stand of the ζ curve the tangents from the point ζ_0 drawn to the ζ curve, at which several of the cases mentioned sub 1—5 and their transition-forms may occur, then we find the following.

A. The saturation-curve of the substance (W) and consequently also the osmotic pressure-curve consists of one single branch.

Then we may get a diagram as in fig. 3, in which the osmotic pressure-curve is represented by $a_0 b_1 u v w b_2 c$; the curves $d_1 b_1 e_1$ and $d_2 b_2 e_2$ are the limit-curves of the region of dimixtion. Starting from a_0 , the osmotic curve comes in b_1 under the pressure P_{b_1} in the region of dimixtion, it reaches in u a maximum- and afterwards in w a minimum-pressure and in b_2 under a pressure $P_{b_2} = P_{b_1}$ it leaves the region of dimixtion. The parts $a_0 b_1$ and $b_2 c$ represent

stable states, the parts b_1u and wb_2 represent metastable states and part uvw unstable states. When the point w is situated below the line $a_0a'_0$, as is drawn in fig. 3, then there are also liquids (unstable and metastable) with negative osmotic pressure.

When we limit ourselves to stable states alone, then only one liquid belongs to each osmotic pressure $\pi = P - P_0$. However the two liquids b_1 and b_2 belong to the osmotic pressure $\pi = P_{b_1} - P_0 = P_{b_2} - P_0$; those liquids are also in equilibrium with one another under the pressure $P_{b_1} = P_{b_2}$.

B. The saturation-curve of the substance (W) and consequently also the osmotic pressure-curve consists of two parts, separated from one another.

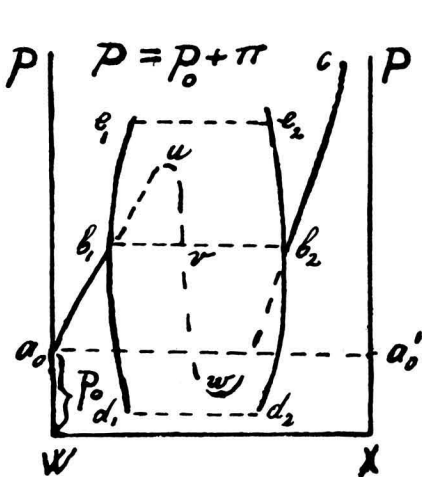


Fig. 3.

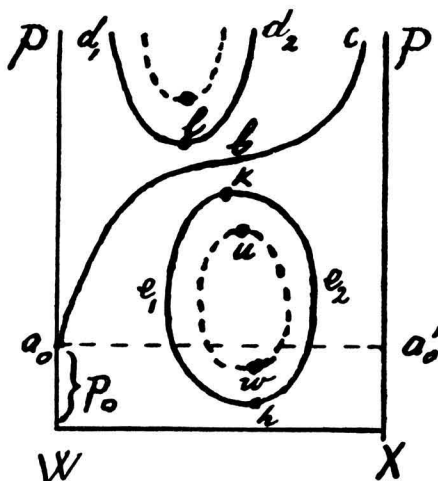


Fig. 4.

Then we may obtain a diagram as in fig. 4, in which the one part of the osmotic pressure-curve is represented by a_0bc , the other part by the closed curve uw . The latter is situated within the region of dimixtion with the limit-curves ke_1h and ke_2h , of which k and h represent the critical points. The part of curve uw , directed towards point e_1 , represents unstable states, the part of this curve directed towards point e_2 , represents metastable states.

The region of dimixtion can be situated also above the curve a_0bc ; this case is represented in fig. 4 by curve d_1ld_2 . The dotted line within this region of dimixtion then represents the second branch of the osmotic pressure-curve.

When we limit ourselves to stable states, then to each definite osmotic pressure $\pi = P - P_0$ belongs one liquid only.

In general the osmotic pressure-curve a_0bc shall ascend only

slowly in the vicinity of the critical point k (or l) with increasing concentration of the not-diffusing substance X . In the point k (or l) itself is viz. $r = 0$; on curve $a_0 b c$, in the vicinity of this point k (or l) r is positive, but it may be still very small. When this is the case, then the above-mentioned follows at once from (5).

Between the figures 3 and 4 a transition-form exists. This occurs when the osmotic pressure-curve $a_0 b c$ comes in contact with one of the regions of dimixtion f.i. kh in the critical point k . Then point u coincides with k . Curve $a_0 b c$ then shows in k a point of inflexion with a horizontal tangent.

Till now we have assumed that the diffusing liquid W , with respect to which we define the osmotic pressure $\pi = P - P_0$ of a liquid L , has a constant external pressure P_0 . Now we shall examine which influence has a change of P_0 on the osmotic pressure π . We take a liquid of constant composition; consequently x in (3) is constant. From (3) now follows:

$$dP = \frac{v_0}{v - x} \frac{\partial v}{\partial x} dP_0 \quad \dots \quad (12)$$

As now $d\pi = dP - dP_0$, we find:

$$d\pi = \frac{v_0 - v + x \frac{\partial v}{\partial x}}{v - x} \frac{\partial v}{\partial x} dP_0 \quad \dots \quad (13)$$

When we bring the pressure of the diffusing liquid W from P_0 to $P_0 + dP_0$, then the change dP of the pressure and the change $d\pi$ of the osmotic pressure of the liquid L are defined by (12) and (13). Consequently in figs. 1, 3 and 4 the straight line $a_0 a'_0$ shifts upwards a part dP_0 , each point of the osmotic pressure-curve a part dP (defined by 12). As, however, dP depends also on x , all points of the osmotic pressure-curve don't shift upwards in the same extent; consequently also this curve changes its form, so that the osmotic pressure changes also. This follows at once also from (13) from which it appears at the same time that the change $d\pi$ of the osmotic pressure depends also on the composition of the liquid.

In the figs. 3 and 4 on change of the pressure P_0 the osmotic curves shift, therefore, while the regions of dimixtion rest on their places of course. In fig. 3 the points b_1 and b_2 shift, therefore, along the curves $d_1 e_1$ and $d_2 e_2$; in fig. 4 the osmotic pressure-curve either approaches more or moves further from the critical point k or l .

On further change of P_0 , the osmotic curve may go now through the point l ; on still more change fig. 4 passes then into fig. 3.

Consequently we find: the osmotic pressure of a liquid L with respect to the diffusing substance W depends on:

1. the concentration of the liquid L .
2. the external pressure P_0 of the diffusing liquid W . It may depend also on this pressure P_0 , whether the osmotic pressure-curve consists of one branch (fig. 3) or of more branches (fig. 4).

As the coefficient of dP_0 in (13) may be as well positive as negative, the osmotic pressure may either grow or diminish. However the osmotic pressure shall grow at increase of P_0 with liquids which contain only little of the not-diffusing substance X .

From (13) and also from (7) it follows viz.:

$$\frac{d\pi}{dP_0} = -\frac{1}{v} \frac{\partial v}{\partial P_0} \cdot \pi = -\frac{RT}{v^2} \frac{\partial v}{\partial P_0} \cdot \pi \dots \dots (14)$$

in which $\frac{\partial v}{\partial P_0}$ is negative of course. As $\frac{\partial v}{\partial P_0}$ is only very small, the change of the osmotic pressure is also very small. With small changes of P_0 the osmotic pressure practically does not change.

VAN 'T HOFF has compared the osmotic pressure of a liquid L with the pressure which the not-diffusing substance X should exert, when in gas-state this should occupy the volume v of the liquid L .

Following this comparison in large lines we might say that in fig. 1 the substance X behaves like a gas, far above its critical temperature T_k , in fig. 4 as a gas, in the vicinity of this temperature and in fig. 3 as below T_k . On branch a, b_1 the substance X should be then in gaseous state, on branch b, c in liquid state. Further we should have to assume that this critical temperature, and, therefore, also the behaviour of the substance X depends on the pressure P_0 of the diffusing substance.

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(To be continued).