

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

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Influence of the temperature and the pressure on osmotic systems.

We take the osmotic equilibrium :

$$E_1 \mid E_2 \dots \dots \dots (1)$$

in which we keep constant the total composition of each of both the separate systems at the left and at the right of the membrane. In order to find the number of licences of this equilibrium, we can use a.o. the membrane-phase-rule. (Comm. VII and VIII) viz.:

an osmotic equilibrium, which contains at the one side of the membrane n_1 components in r_1 phases and at the other side n_2 components in r_2 phases, has, when there are d diffusing substances:

$$n_1 + n_2 - (r_1 + r_2) + 3 - d \dots \dots \dots (2)$$

licences. If there is one diffusing substance only, as in the cases which we considered till now, then the osmotic equilibrium has, therefore:

$$n_1 + n_2 - (r_1 + r_2) + 3 - 1 = (n_1 - r_1 + 2) + (n_2 - r_2 + 2) - 2 \quad (3)$$

licences. Consequently we can say:

the number of licences of an osmotic equilibrium with one diffusing substance is equal to the sum of the licences of both the separate systems, diminished with two.

If we keep constant, as in (1), the total composition of each of the separate systems, then each has two licences, viz. the temperature and the pressure; consequently the osmotic equilibrium (1) has $2 + 2 - 2 = 2$ licences.

We now take the osmotic equilibrium:

$$[(E_1)_{P_1} \mid (E_2)_{P_2}]_T \dots \dots \dots (4)$$

in which at the temperature T a pressure P_1 is at the left of the membrane and a pressure P_2 at the right. Of the three variables, viz. $P_1 P_2$ and T we may take two arbitrarily, therefore. If we change the temperature with dT and the pressures at the left and the right of the membrane with dP_1 and dP_2 then (4) passes into the osmotic system:

$$[(E_1)_{P_1+dP_1} \mid (E_2)_{P_2+dP_2}]_{T+dT} \dots \dots \dots (5)$$

Then the *O.W.A.* at the left and at the right side of the membrane has increased with:

$$d\xi_1 = \Delta H_1 \cdot dT - \Delta V_1 \cdot dP_1 \quad d\xi_2 = \Delta H_2 \cdot dT - \Delta V_2 \cdot dP_2. \quad (6)$$

in which ΔH_1 and ΔV_1 represent the osmotic increase of entropy and volume of the system E_1 ; ΔH_2 and ΔV_2 represent the same for the system E_2 .

In order to keep equal the *O.W.A.* on both sides of the membrane, we must satisfy, according to (6):

$$(\Delta H_1 - \Delta H_2) dT = \Delta V_1 \cdot dP_1 - \Delta V_2 \cdot dP_2 \dots \dots (7)$$

from which appears, in accordance with above, that we may take arbitrarily two of the three increments.

With the aid of (7) we are able to deduce different properties. Previously we have deduced a.o. that we can change the pressure on both sides of the membrane in an osmotic equilibrium at constant temperature; those changes in pressure dP_1 and dP_2 must satisfy then formula (5) of communication XX, viz.:

$$\Delta V_1 \cdot dP_1 = \Delta V_2 \cdot dP_2 \dots \dots \dots (8)$$

which also follows at once from (7) if we put herein $dT = 0$.

As special case of (4) we may also take the osmotic equilibrium:

$$(E_1 \mid E_2)_{P, T} \dots \dots \dots (9)$$

in which the pressure is the same on both sides of the membrane; as by this the number of licences decreases with one, (9) therefore, has instead of two, one licence only. Consequently to each temperature T belongs a definite pressure P of the osmotic equilibrium; we are able to represent, therefore, the connection between temperature and pressure in a PT -diagram by a curve, which we shall call „the PT -curve of the osmotic equilibrium”; in fig. 1 such a curve is represented by aua_1 . An arbitrary point u of this curve indicates, therefore, that at the temperature $T_u = Ou_1$ the pressure on both sides of the membrane must be $P_u = u_1 u$ and reversally, that we must take a temperature $T_u = Ou_1$ when the pressure on both sides of the membrane is $P_u = u_1 u$.

The direction of this PT -curve follows from (7); if we put viz. $dP_1 = dP_2 = dP$ then we find:

$$\frac{dT}{dP} = \frac{\Delta H_1 - \Delta H_2}{\Delta V_1 - \Delta V_2} = \frac{\Delta H_2 - \Delta H_1}{\Delta V_2 - \Delta V_1} \dots \dots \dots (10)$$

If we represent the heat of diffusion and the osmotic increase of volume at the transition of a little water from system E_2 towards E_1 (or from E_1 towards E_2) by $Q_{2.1}$ and $V_{2.1}$ (or $Q_{1.2}$ and $V_{1.2}$), then (10) passes into:

$$T \frac{dP}{dT} = \frac{Q_{2.1}}{V_{2.1}} = \frac{Q_{1.2}}{V_{1.2}} \dots \dots \dots (11)$$

which formula has the same form as that of CLAPEYRON; however, the magnitudes occurring in the second part have another meaning.

It numerator and denominator in (10) or (11) have the same sign, then the pressure of the osmotic equilibrium increases with increase of temperature; then the PT -curve is a curve, ascending with the temperature, as curve $a a_1$ in fig. 1 or branch $a u b$ in fig. 2. If numerator and denominator have opposite sign, then the pressure decreases with increase of T ; then the PT -curve is a curve, descending with the temperature, as branch $a_1 v b$ in fig. 2. If the numerator becomes zero, then the pressure is maximum or minimum; if the denominator becomes zero, then the temperature is maximum or minimum. In fig. 2 the temperature is a maximum in b ; consequently the osmotic equilibrium (9) cannot exist, above this temperature T_b . If we heat it notwithstanding above this temperature T_b , then, therefore, water must diffuse in any direction and another osmotic equilibrium must be formed; we shall refer to this later.

In order to apply our considerations to a definite case we take instead of (9) the osmotic equilibrium:

$$[Y + L \mid L_s]_{P, T} \dots \dots \dots (12)$$

in which at the left side of the membrane the binary system $Y + L$ and on the right side a ternary liquid L_s . If we assume that fig. 1, III is valid for a definite P and T of (12), then the liquid at the left of the membrane has the composition w ; the liquid s at the right of the membrane is represented then by a point of the isotonic curve $w m$ (fig. 1, III). If we represent the $O.W.A.$, the osmotic increase of entropy and volume of the left system by ξ , ΔH and ΔV and those of the liquid s by ξ_s , ΔH_s and ΔV_s , then we have:

$$d\xi = \Delta H \cdot dT - \Delta V \cdot dP \quad d\xi_s = \Delta H_s \cdot dT - \Delta V_s \cdot dP \quad (13)$$

The direction of the P, T -curve of (12) is then defined by:

$$\frac{dP}{dT} = \frac{\Delta H - \Delta H_s}{\Delta V - \Delta V_s} \dots \dots \dots (14)$$

Of the many imaginable cases we shall discuss only some; for this we shall assume that ΔV_s , ΔH_s and ΔH are positive and that $\Delta H > \Delta H_s$; the numerator of (14) is then always positive. Further we distinguish the two cases:

A. ΔV is always positive and greater than ΔV_s .

B. If we represent the composition of the liquid L , saturated with solid Y by: $y \text{ Mol } Y + (1-y) \text{ Mol. water}$, then for small values of y ΔV is positive and larger than ΔV_s ; for greater values of y , however, ΔV is negative. Previously we found (formula 10^a of Communication XIX) for ΔV :

$$\Delta V = \frac{V - yV_y}{1 - y} \dots \dots \dots (15)$$

in which V and V_y represent the molecular volumina of the liquid L and of the solid substance Y . From this and from the considerations in

Communication XIX it appears that the case *A* can occur only then, when the solid substance *Y* melts with increase of volume, and case *B* when this melting takes place with decrease of volume.

A. In the case *A* numerator and denominator of (14) are always positive; consequently the *PT*-curve of the osmotic equilibrium (12) is a curve ascending with the temperature, f.i. curve *aa*₁ of fig. 1. In order

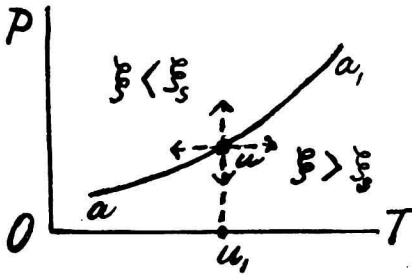


Fig. 1.

to keep the system (12) in osmotic equilibrium with increase of temperature we also have to increase the pressure on both sides of the membrane.

As, therefore, the osmotic equilibrium (12) only exists at temperatures and under pressures, which are represented by points of the *PT*-curve, we may put the question: what will take place, if we choose

a temperature and a pressure, which are represented by a point which is not situated on the *PT*-curve. Let us take the osmotic equilibrium:

$$[Y + L \mid L_s]_{p_u, T_u} \dots \dots \dots (16)$$

which is represented in fig. 1 by the point *u* of the *PT*-curve *aa*₁. While the pressure remains constant, we bring the temperature to *T*_u + *dT*; we then have the osmotic system:

$$[Y + L \mid L_s]_{p_u, T_u + dT} \dots \dots \dots (17)$$

which is represented in fig. 1 by a point in the vicinity of *u* and on a horizontal line going through this point *u*. We may imagine this point, which we shall call *u'*, in one of the extreme points of the horizontal arrows, drawn through point *u*; for *dT* > 0 *u'* is situated at the right, for *dT* < 0 at the left of the point *u*.

As *dP* is zero in the point *u'*, it follows from (13) for the change of the *O.W.A.* at the left and the right of the membrane:

$$d\xi = \Delta H \cdot dT \quad d\xi_s = \Delta H_s \cdot dT \dots \dots \dots (18)$$

in which, according to our assumption $\Delta H > \Delta H_s$. Consequently, as is indicated also in fig. 1, for *dT* > 0 is: $\xi > \xi_s$; for *dT* < 0 is $\xi < \xi_s$.

If we bring, while the temperature remains constant, the pressure to *P*_u + *dP*, then we have the osmotic system:

$$[Y + L \mid L_s]_{p_u + dP, T_u} \dots \dots \dots (19)$$

which is represented in fig. 1 by a point in the vicinity of *u* and in one of the extreme points of the vertical arrows, drawn through point *u*. As now *dT* is zero, follows from (13) for the change of the *O.W.A.* at the left and at the right of the membrane:

$$d\xi = -\Delta V \cdot dP \quad d\xi_s = -\Delta V_s \cdot dP \dots \dots \dots (20)$$

in which, in accordance with our assumption is $\Delta V > \Delta V_s$. For $dP > 0$ is, therefore, $\xi < \xi_s$ and for $dP < 0$ is $\xi > \xi_s$.

We may summarise this and the previous in the following way. If in the osmotic system :

$$[Y + L \mid L_s]_{P', T'} \dots \dots \dots (21)$$

P' and T' are a pressure and a temperature, which are represented:

1. by a point of the PT -curve, then the system is in osmotic equilibrium and nothing happens;
2. by a point at the right or below the PT -curve (fig. 1) then is $\xi > \xi_s$ and consequently water diffuses from right to left;
3. by a point at the left or above the PT -curve (fig. 1) then is $\xi < \xi_s$ and consequently water diffuses from left to right.

This diffusion of water, with which each of both the separate systems changes its total composition, continues till the *O.W.A.* on both sides of the membrane, is equal again.

B. As, according to our supposition, the denominator of (14) is positive for small values of y , therefore, at low temperature and pressure, but negative with greater values of y , this must be zero in a definite point b of the PT -curve, consequently at a definite temperature T_b and under a pressure P_b . Therefore, the PT -curve has in the point b a vertical tangent and consequently it consists of a branch ab , ascending with the temperature and of a branch $a_1 b$ descending with the temperature (fig. 2). On branch ab is $\Delta V > \Delta V_s$ and consequently the denominator of (14) is positive; on branch $a_1 b$ is $\Delta V < \Delta V_s$ and consequently the denominator of (14) is negative.

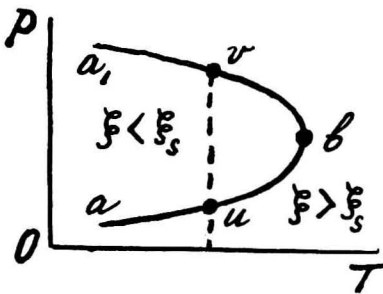


Fig. 2.

Therefore, the osmotic equilibrium (12) can exist no more at temperatures higher than T_b ; at lower temperatures it can

occur at every temperature under two different pressures.

In a similar way as above we now deduce with the aid of (18) and (20): if in the osmotic system :

$$[Y + L \mid L_s]_{P', T'} \dots \dots \dots (22)$$

P' and T' are a temperature and pressure, which are represented:

1. by a point of the PT -curve, then the system is in equilibrium and nothing happens;
2. by a point outside the PT -curve (fig. 2), then is $\xi > \xi_s$ and consequently water diffuses from right to left;
3. by a point within the PT -curve (fig. 2), then is $\xi < \xi_s$ and consequently water diffuses from left to right.

We are able to deduce the above also in another way, f.i. with the

aid of the $P\xi$ -diagram, which we have already discussed in Communication XXI. The system $Y+L$ has viz. at each T and P a definite ξ ; if we change either the T or the P , then, therefore, also changes the ξ viz. the $O.W.A.$ Under constant pressure we are able to represent the connection between the T and the $O.W.A.$ in a $T\xi$ -diagram by a curve, which we may call the " $T\xi$ -curve" of the system. If we keep the temperature constant, then we can represent in a $P\xi$ -diagram the relation between the pressure and the $O.W.A.$; we then get the $P\xi$ -curve of the system.

In fig. 1, XXI is represented the $P\xi$ -curve of a system $Y+L$ by curve $cf l$; this is deduced in the supposition that the osmotic increase of volume ΔV of this system is positive under lower pressures, that it is zero in the point f and negative under higher pressures. As this supposition is the same as in the case B , discussed above, the $P\xi$ -curve in this case B will have also a form as curve $cf l$ in fig. 1, XXI; in fig. 4 is drawn also a similar curve $cf l$.

If, however, as we have done in case A , we assume that ΔV is always positive, then follows, as $d\xi = -\Delta V \cdot dP$, that the $P\xi$ -curve is a curve, descending with the pressure, as curve cul in fig. 3.

We now shall indicate in those figs. 3 and 4 also the $P\xi$ -curve of the liquid L_s ; as, according to our supposition, ΔV_s is positive, it is also a curve, descending with the temperature; in both figures it is represented by the dotted curve st .

A . In the case mentioned above sub A fig. 3 is valid, in which u is the point of intersection of the two $P\xi$ -curves; of course this figure is valid only for a definite temperature, which we shall call T_u . The change of the $O.W.A.$ of the system $Y+L$ and that of the liquid L_s is defined at constant temperature by:

$$d\xi = -\Delta V \cdot dP \quad d\xi_s = -\Delta V_s \cdot dP \quad . \quad . \quad . \quad (23)$$

in which, according to our supposition $\Delta V > \Delta V_s$; hence follows that on

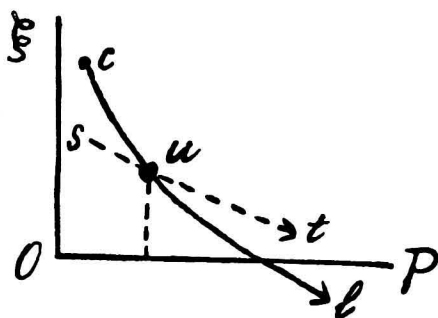


Fig. 3.

the right side of the point of intersection branch ul is situated below branch ut (viz. $\xi < \xi_s$) and on the left side of this point curve cu is situated above su (viz. $\xi > \xi_s$); consequently both curves are situated with respect to one another as is drawn in fig. 3 and they have only one point of intersection, therefore. This point, in which is $\xi = \xi_s$, represents the pressure

$P_u = Oz$, belonging to the temperature T_u , under which the $O.W.A.$ is the same on both sides of the membrane; consequently T_u and P_u are corresponding temperature and pressure of the PT -curve of the osmotic equilibrium (12); they are represented in fig. 1 by point u .

If we take in fig. 3 a pressure smaller than $P_u = Oz$, then is, as branch cu is situated above su , $\xi > \xi_s$; for pressures greater than P_u follows $\xi < \xi$. Going in fig. 1 from point u towards lower pressures, we must arrive in the field, where is $\xi > \xi_s$; going towards higher pressures, we must arrive in a field, where is $\xi < \xi_s$. This is in accordance with the position of both fields, which we have deduced already above in another way.

As we have seen already above, fig. 3 is only valid for a definite temperature, which we called T_u . If we bring the temperature to $T_u + dT$, then both the $P\xi$ -curves change a little their position and form; from (13) follows for constant pressure:

$$d\xi = \Delta H \cdot dT \quad d\xi_s = \Delta H_s \cdot dT \quad . \quad . \quad . \quad (24)$$

by which the vertical shifting of each point of both the curves is defined. As ΔH and ΔH_s both are positive, both curves shift towards above, therefore, with increase of temperature; as, according to our supposition $\Delta H > \Delta H_s$, each point of curve cl , therefore, shifts somewhat more towards above than the corresponding point of curve st ; the point of intersection u of the two curves is displaced, therefore, a little towards the right, consequently towards a higher pressure. Hence appears, therefore, that in case *A* the pressure of the osmotic system increases with increase of temperature; in accordance with previously we find, therefore, that the PT -curve consists of a curve ascending with the temperature, as in fig. 1.

B. In the case, mentioned sub *B* is valid fig. 4, in which both the $P\xi$ -curves intersect one another in the two points u and v ; just as above we find that both curves are situated with respect to one another as is drawn in fig. 4; the left point of intersection u is situated always between c and f ; the right point of intersection v can be situated as well between u and f as between f and l .

As in each of both points of intersection $\xi = \xi_s$, therefore at the temperature, for which fig. 4 is valid, two pressures P_u and P_v exist, under which the osmotic equilibrium (12) can exist; this is in accordance also with fig. 2, in which u and v represent the corresponding points u and v of fig. 4.

If we take in fig. 4 a pressure smaller than P_u or greater than P_v , then is, as appears from the position of both curves, $\xi > \xi_s$; if we take a pressure between P_u and P_v then we see that $\xi < \xi_s$. Consequently in fig. 2 we must have a field, in which $\xi > \xi_s$ below point u and above point v ; between point u and point v must be situated a

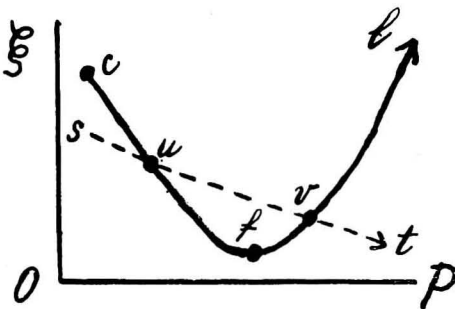


Fig. 4.

field, in which $\xi < \xi_s$; this is in accordance with the position of those fields, which we have deduced above already.

As, with increase of temperature, both curves of fig. 4 shift towards above, but each point of curve cf more than the corresponding point of curve st , the point of intersection u must be removed towards the right and the point of intersection v towards the left. With increase of T , therefore, a temperature comes, at which the two curves touch one another in a point b , situated between c and f . In accordance with fig. 2 we find, therefore, that a definite temperature T_b exists, at which the osmotic system (12) can exist still only under one single pressure, viz. P_b .

If we raise the temperature still further, then the two $P\xi$ -curves do no more intersect one another; consequently the osmotic equilibrium can exist no more. In accordance with fig. 2 also appears that $\xi > \xi_s$, so that (12) now is an osmotic system, in which water will diffuse from left to right as long as till a new system is formed, in which the *O.W.A.* is equal on both sides of the membrane.

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(To be continued).
