Chemistry. — *Osmotic systems in which non-diffusing substances may occur also.* IV. By F. A. H. SCHREINEMAKERS.

IV. *Systems with elastic walls and membranes.*

In the preceding communications we discussed osmotic systems, in which the pressure remains constant on both sides of the membrane, or in which each of the two liquids was enclosed in a space of constant volume; further we assumed that the membrane was inextensible. As, however, Nature has osmotic systems enclosed in spaces with extending walls and membranes, we shall also briefly discuss these systems.

We now take an osmotic system as in fig. 1, in which for the present we overlook the letters P_0 and P'_0. On the left side of the membrane, which
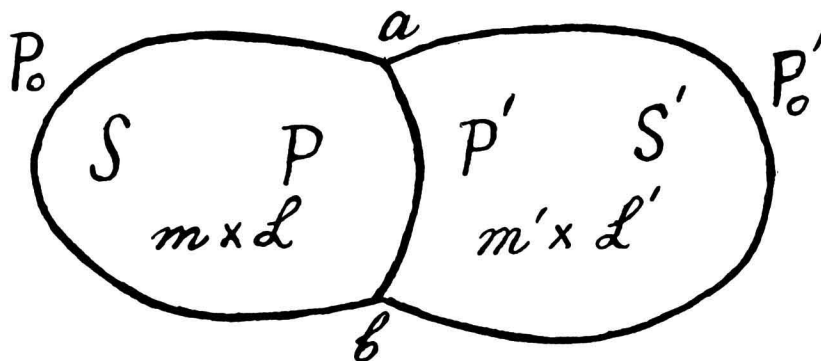

Fig. 1

is represented by the curved line ab, is a space S; on the right side is a space S'.

By the wall of space S (or S') the entire wall of this space, except the part formed by the membrane, is meant; we now assume that the walls of these spaces and the membrane are elastically extensible.

We imagine space S filled with m quantities of a liquid L under the pressure P, space S' with m' quantities of a liquid L' under the pressure P'.

Of course these spaces S and S' may have all sorts of shapes, which depends on their walls being completely or only partially extensible, on the elasticity in different directions, etc. It may be imagined among other things that the walls extend principally in one direction only, as may be the case with growing cells of plants.

For the sake of simplicity we now shall represent the system of fig. 1 by:

$$\left._s^r\left(m \times L\,(d+n)_P \right)_b^a m' \times L'\,(d+n')_{P'} \right)_{s'}^{r'} \quad \ldots \quad \textbf{(1a)}$$

in which the curvature of the lines ab, rs and $r's'$ indicate that the membrane and the walls of the spaces S and S' are elastically extensible; inextensible membranes and walls will be represented by straight lines.

If we imagine the wall of one of the spaces e.g. of S, inextensible, then we get the system:

$$\left._s^r\left| m \times L\,(d+n)_P \right)_b^a m' \times L'\,(d+n')_{P'} \right)_{s'}^{r'} \quad \ldots \quad \textbf{(2a)}$$

When the walls of the two spaces become inextensible, we get:

$$\left._s^r\left| m \times L\,(d+n)_P \right)_b^a m' \times L'\,(d+n')_{P'} \right|_{s'}^{r'} \quad \ldots \quad \textbf{(3a)}$$

We now may imagine the membrane to be inextensible also in each of the systems $(1a)$—$(3a)$; then we shall call them $(1b)$—$(3b)$.

We are now going to call a variable space, a space, the volume of which can change because of the elasticity of wall or membrane or of both; a space, the volume of which does not change, is called invariant. Then each of the systems $(1a)$, $(2a)$, $(3a)$ and $(1b)$ has two variable spaces; system $(2b)$ has one variable and one invariant space and system $(3b)$ has two invariant spaces.

We now take a variable space with a given wall and a given membrane, so that between the volume and the pressure P within this space a relation

$$\varphi\,(P\,.\,V) = 0 \quad \ldots \ldots \ldots \quad \textbf{(4)}$$

exists; with every pressure P the volume V and reversally with every volume V the pressure P will then be defined. We shall call such a variable space: "definite variable".

When there is besides an external pressure on the wall of this space, it will also occur in (4); the same obtains for the pressure which the liquid of the other space brings to bear on the membrane, when it is extensible. The function φ, which contains among other things also the magnitudes, determining the elasticity of space or membrane or of both, is generally unknown; we may assume, however, that the volume of this space will increase when the pressure inside this space increases.

When in a system the osmosis is over and this system has consequently attained on equilibrium, then, as we have mentioned already in preceding Comm., the d equations:

$$O\,A = (O\,A)' \quad \ldots \ldots \ldots \ldots \quad \textbf{(5)}$$

obtain, expressing that each of the d diffusing substances has the same *O.A.* viz. the same osmotic attraction on both sides of the membrane. In order to deduce this for the general case of system (1a), we imagine this represented again by fig. 1 ; we assume here that an external pressure P_0 is brought to bear on the wall of space S and an external pressure P_0' on the wall of space S'.

When dm quantities of one of the diffusing substances travel through the membrane towards the left, then the volumes V and V' of each of the two spaces will change a little ; now we assume :

1. the wall of space S moves outwards over a volume dv; by this I mean that the volume between the new and the old position of this wall is dv.

2. the membrane moves towards the right over a volume dv_1.

3. the wall of the space S' moves inwards over a volume dv'.

Then the volumina V and V' increase with

$$dV = dv + dv_1 \quad \text{and} \quad dV' = -(dv_1 + dv') \ . \ \ . \ \ . \ \ (6)$$

If we now represent the entire free energy of the two liquids by ψ and ψ', that of the two walls by ψ_r and ψ'_r and that of the membrane by ψ'_m, then

$$d(\psi + \psi' + \psi_r + \psi'_r + \psi_m) + P_0\,dv - P'_0\,dv' = 0 \ . \ \ . \ \ . \ (7)$$

must be satisfied, in which the two last terms indicate the external work performed by the system. We now have :

$$d\psi = \left(\frac{\partial \psi}{\partial m}\right)_V dm + \left(\frac{\partial \psi}{\partial V}\right)_m dV = \left(\frac{\partial \psi}{\partial m}\right)_V dm - P(dv + dv_1) \ . \ \ . \ \ (8)$$

As the liquid of space S' gives off the dm quantities of the diffusing substance, it follows :

$$d\psi' = -\left(\frac{\partial \psi'}{\partial m}\right)_V dm + P'(dv_1 + dv') \ . \ \ . \ \ . \ \ . \ (9)$$

If we take into consideration the work, performed on the wall of space S and through the wall of space S', we find :

$$d\psi_r = (P - P_0)\,dv \quad \text{and} \quad d\psi'_r = -(P' - P'_0)\,dv' \ . \ \ . \ \ . \ (10)$$

For the change in the free energy of the membrane we find :

$$d\psi_m = (P - P')\,dv \ . \ \ . \ \ . \ \ . \ \ . \ \ . \ \ . \ (11)$$

If we substitute (8)—(11) in (7) then we find that

$$\left(\frac{\partial \psi}{\partial m}\right)_V = \left(\frac{\partial \psi'}{\partial m}\right)_{V'} \ . \ \ . \ \ . \ \ . \ \ . \ \ . \ \ . \ (12)$$

must be satisfied.

This means that the diffusing substance must have the same thermodynamical potential in both liquids. As this obtains for each of the d diffusing substances and as the *O.A.* of a substance is equal to its potential with the negative sign, it appears that for equilibrium (1) the d equations (5) are valid. So the same also obtains for the equilibria, which can be deduced from (1).

Liquid L contains $d + n$ substances, so that its composition is determined by $d + n - 1$ concentrations; if we add to this also the quantity m, the pressure P and the volume V, then the left-side liquid contains, therefore, $d + n + 2$ variables. As liquid L' contains $d + n'$ substances, both liquids will contain together

$$2d + n + n' + 4 \text{ variables} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we represent the volume of one quantity of liquids L and L' by v and v', we have:

$$V = mv \quad \text{and} \quad V' = m'v' \quad . \quad . \quad . \quad . \quad . \quad (14)$$

as $v(v')$ depends upon the composition and the pressure of liquid $L(L')$, both these equations contain together all variables.

Now we imagine that the spaces of the systems are either "definite variable" or "invariant". Then two equations (4) obtain for the systems $(1a)$, $(2a)$, $(3a)$ and $(1b)$, which will then have two "definite variable" spaces. For system $(2b)$ in which S' is "definite variable" and S is "invariant", then one of the relations (4) will obtain and $V = $ constant. For system $(3b)$, in which both spaces are invariant, $V = $ constant and $V' = $ constant obtain. So for each of these systems two relations obtain, which we shall call $(14a)$.

If we now imagine that these systems have attained equilibrium, so that the d equations (5) are valid too, then $d + 4$ relations exist between the variables, therefore; from this it follows:

A. a free Q-equilibrium with "definite variable" or "invariant" spaces has:

$$d + n + n' \text{ freedoms} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Here, just as in the preceding communications, we mean by a free Q-equilibrium an equilibrium in which the quantity of each of the substances present can still be changed arbitrarily.

In a Def. Q-equilibrium, however, the quantity of each of the diffusing and non-diffusing substances has a definite invariable value. Then there are d relations, expressing that the quantity of each of the d diffusing substances has a given value; n relations expressing the same for the n non-diffusing substances on the left side and n' relations, expressing the same for the n' non-diffusing substances on the right side of the membrane

(compare also the preceding communications). As there still exist, therefore

$$d + n + n' \text{ relations,}$$

it follows :

B. a Def. Q-equilibrium with definite variable or invariant spaces has no freedoms. The volumina V and V', the pressures P and P', the quantities m and m' and the compositions of the two liquids L and L' are completely defined.

In Comm. II and III the influence, which the change in the permeability of a membrane can have upon the state of an equilibrium, has been discussed. If we now consider the change in the elasticity of the membrane or of the walls as well, we find :

C. in a Def. Q-equilibrium with definite variable or invariant spaces every change in the membrane, by which this becomes more or m.l. permeable, and every change in the elasticity of the membrane or of the walls also causes a change in the e-state; each of the changes is then followed by an osmosis until the new e-state has set in.

Here we mean by e-state the state of equilibrium of the system.

We now take an osmotic system :

$$\left._s^r\!\!\left(m_0 \times L_0 \right)_a^a inv. L_i \left(d + n'\right)_{P_i} \right. \quad . \quad . \quad . \quad . \quad (16)$$

in which on the right side of the membrane ab is an invariant liquid i under the pressure P_i; on the left side is a definite variable space S filled with m_0 quantities of a liquid L_0; we assume that this liquid contains n non-diffusing and an arbitrary number of diffusing substances. If we now leave this system alone, the n non-diffusing substances will of course remain in space S; system (16) then passes into an equilibrium :

$$\left._s^r\!\!\left(m \times L \left(d + n\right)_P \right)_b^a inv. L_i \left(d + n'\right)_{P_i} \right. \quad . \quad . \quad . \quad . \quad (17)$$

in which liquid L now contains the same d diffusing substances as liquid i. If namely one or more of these d substances were not yet present in L_0, they would certainly enter into it during the osmosis. If in L_0 other diffusing substances were present besides those in liquid i, then they will divide themselves between the two liquids; as, however, liquid i is kept invariant, these substances are being taken away continuously, so that at last they will disappear from the system.

In nature such systems may occur e.g. when some liquid or other flows along the membrane keeping practically the same composition, and when space S has been filled with a tissue; the film in which this tissue is enclosed then forms the wall of this space.

It is clear that (7) cannot be a Def. Q-equilibrium (compare also Comm.

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III) ; here namely we can only consider the quantity of each of the n non-diffusing substances as given ; we now shall call an equilibrium, containing a definite quantity of each of the n non-diffusing substances, a Def. $Q. n.$-equilibrium. We now find :

D.   a Def. $Q.n.$-equilibrium with one definite variable or invariant space and with an invariant liquid has no freedoms ; each change in the membrane, by which this becomes more or m.l. permeable, and each change in the elasticity of membrane or wall also causes a change in the e-state of the space ; every change is followed by an osmosis until the new e-state has set in.

In order to illustrate the preceding considerations, we take the equilibrium

$$\overset{r}{\underset{s}{\left(}} m \times L \, (W + X)_P \, \Big|_b^a \, inv. \, L_i \, (W + X + \overline{Y})_{P_i} \quad . \quad . \quad . \quad (18)$$

with a definite variable space S ; of course the membrane ab may also be supposed to be extensible here. The membrane is, as has been indicated by a horizontal dash over Y, impermeable for Y and, therefore, permeable for W and X only ; from this it follows $P < P_i$.

When the membrane now becomes permeable for Y too and hence for all substances, a new equilibrium can arise only then, when the two liquids will get the same pressure and composition ; so (18) passes into :

$$\overset{r}{\underset{s}{\left(}} m_1 \times L_i \, (W + X + Y)_{P_i} \, \Big|_b^a \, inv \, L_i \, (W + X + Y)_{P_i} \, . \quad . \quad (19)$$

During the transition from (18) into (19) not only Y but also water and X will pass through the membrane. As the pressure within space S in (19) is now greater than in (18) (viz. $P_i > P$), the volume of S will increase at the transition of (18) into (19).

If, however, we take the equilibrium

$$\overset{r}{\underset{s}{\left(}} m \times L \, (W + X + \overline{Y})_P \, \Big| \, inv \, L_i \, (W + X)_{P_i} \quad . \quad . \quad . \quad (20)$$

then is $P > P_i$. When the membrane now becomes permeable for Y also, then (20) passes into :

$$\overset{r}{\underset{s}{\left(}} m_1 \times L_i \, (W + X)_{P_i} \, \Big| \, inv \, L_i \, (W + X)_{P_i} \quad . \quad . \quad . \quad (21)$$

During this transition the volume of space S now will decrease.

If in (18) and (20) we imagine instead of space S a tissue enclosed by an elastic film, then at the transition of (18) into (19) this tissue will swell to a definite volume and perhaps it will burst. During the transition from (20) into (21) this tissue will contract to a definite volume. The same

will take place also when we bring these tissues into such a large quantity of liquid *i*, that the composition of this liquid will practically change only a little.

We may imagine also that the wall of a space partly loses its elasticity through some influence or other; then this wall will put a smaller pressure on the liquid at the same volume; we may imagine also that at the same time the change in the permeability of the membrane discussed above, occurs as well. A closer consideration of these cases is left to the reader.

(To be continued).

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Chemistry. — *The Exact Measurement of Specific Heats at Higher Temperatures. XI. On the Variability of the Specific Heats of Fused and Solidified Silver under different Circumstances.* By F. M. JAEGER, E. ROSENBOHM and W. A. VEENSTRA.

(Communicated at the meeting of March 25, 1933).

§ 1. In the course of our previous work on the specific heats of stabilized and preliminarily worked metals, some unexplained pecularities in the behaviour of fused and solidified *silver*[1]) were observed, which made it desirable again to study this metal at higher temperatures more in detail. On repeating our measurements of the mean specific heats $\bar{c}_p$ with a lump of silver *B* fused and solidified in air[2]), but being afterwards preserved at room-temperature during five or six months, — the remarkable fact was stated that all values of $\bar{c}_p$, measured by means of the same instrument as formerly used, proved to be *appreciably diminished*. The deviations from the values previously found were in all cases much greater than could be accounted for by the possible experimental errors (see curve *B'* in Fig. 1). Originally we thought that the stabilized lump of silver, by its long preservation at room-temperature had, in some way or other, returned to a less stable condition, — such as, for instance, was met with in the case of cold-plated and laminated silver (curve *P* in Fig. 1). Soon,

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1) F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Proceed. R. Acad. Sciences Amsterdam, **35**, (1932), 768; Recueil d. Trav. d. Chim. Pays-Bas, **52**, (1933), 74; conf. Note 13) at the bottom of page 77, loco cit., on the more rapid increase of $\bar{c}_p$ above 600° – 700° C.

2) On page 74, loco cit., it was erroneously mentioned, that the lump of silver used was fused and solidified "in a vacuum": really it occurred *in air*.