Chemistry. — "*Equilibria in systems, in which phases, separated by a semi-permeable membrane*" IX. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of May 30, 1925).

Two ternary systems.

We take an osmotic equilibrium:

$$E = E_1 \,\vdots\, E_2$$

in which the separate parts E_1 and E_2 are both ternary systems. Of course they have always one component in common, viz. the diffusing substance W (water); both the other components can be either the same or different. Consequently we distinguish three cases:

1. There are three common components; then each of the separate systems contains f.i. the substances $W + X + Y$.

2. There are only two common components; then the one system contains f.i. the substances $W + X + Y$ and the other system the substances $W + X + Z$.

3. There is only one common component, viz. the diffusing substance W. Then the one system contains f.i. the substances $W + X + Y$ and the other system the substances $W + Z + U$.

In previous communications we have discussed already several examples of the first case; now we shall consider some examples of the other cases.

Both the systems contain two common components.

We represent the phases of the system E_1, which contains the components $W + X + Y$ by points of a triangle WXY; those of a system E_2, which contains the components $W + X + Z$ by points of a triangle WXZ. In fig. 1 both triangles are placed against one another with the side WX, they are united in a single diagram.

It appears from the figure that we have assumed that in the system $W + X + Y$ both the components X and Y occur as solid phases; in the system $W + X + Z$, however, only the solid substance X. The saturation-curves of those systems are represented by the curves *ab*, *db* and *dg*. In accordance with the previous the arrows indicate the direction in which the O.W.A. of the saturated liquids increases.

We consider, just as formerly, the osmotic equilibrium:

$$E = E_1 \,\vdots\, E_2 \quad \ldots \ldots \ldots \quad (1)$$

again at constant temperature and under constant pressure; we assume again that the pressure P_1 of system E_1 is equal to the pressure P_2 of system E_2. Then follows from the membrane-phase-rule (Comm. VII):

$$\text{number of freedoms} = 3 + 3 - (r_1 + r_2) - 1 = 5 - (r_1 + r_2) \quad . \quad (2)$$

in which r_1 indicates the number of phases of E_1 and r_2 that of E_2.

In the osmotic equilibrium:

$$E = L_1 \mid L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

L_1 and L_2 represent two liquids. If we take a binary liquid L_q, represented by point q of the side WX, then all liquids of the system $W+X+Y$, which are isotonic with L_q are represented by points of the isotonic curve qq_1; all liquids of the system $W+X+Z$ by an isotonic curve qq_2.

Consequently the two isotonic curves qq_1 and qq_2 start from point q; the one is situated in triangle WXY, the other in triangle WXZ. Each liquid of curve qq_1, therefore, is not only isotonic with each other liquid of this curve, but also with all liquids of curve qq_2.

Generally, therefore, with each liquid, which contains the components $W+X+Y$ is isotonic not only a series of liquids with the same components, but also a series of liquids with the components $W+X+Z$.

Consequently two isotonic curves start from each point of the side WX; we call them conjugated isotonic curves; some of them are dotted in fig. 1. Liquid r_1 is isotonic, therefore, with the liquids L_t, L_d, L_v and L_{r2}; liquid a with the liquids L_c, L_e, L_u and L_h; etc. The binary $W+Y$-containing liquid r_1 is isotonic, therefore, with the binary $W+Z$-containing liquid r^2; etc.

Also follows from the above considerations that the osmotic equilibrium (3) has three freedoms. If we take f.i. for L_1 a definite liquid, f.i. L_t, then two freedoms disappear, consequently L_2 has left still one freedom; it is represented by a point of the conjugated isotonic curves dr_1 and dr_2. We are able to represent this (compare f. i. previous communications) by:

$$E = L_t \mid L\,(1 - dr_1 - dr_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

from which it appears that the liquid L has one freedom and is represented by a point of the conjugated curves dr_1 and dr_2.

If we represent the thermodynamical potential and the composition of liquid L_1 by

$$\zeta_1 \text{ and } x_1X + y_1Y + (1 - x_1 - y_1)W \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

and those of L_2 by:

$$\zeta_2 \text{ and } x_2X + z_2Z + (1 - x_2 - z_2)W \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

then is valid for equilibrium (3) the equation:

$$\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} = \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - z_2 \frac{\partial \zeta_2}{\partial z_2} \quad . \quad . \quad . \quad . \quad (5)$$

As in (5) four variables occur, it also follows from this that the osmotic equilibrium (3) has three freedoms. This also follows at once from (2), if we put herein $r_1 = 1$ and $r_2 = 1$.

If we bring in osmotic contact the liquids L_s and L_u (fig. 1) then, as the O.W.A. of L_u is larger than that of L_s, water shall diffuse from L_s towards L_u. Therefore, liquid L_s moves along the straight line Ws, away from point W, liquid L_u along the straight line uW towards W. This diffusion continues till both liquids have got the same O.W.A., therefore, till both come on conjugated isotonic curves. When this is f. i. the case on the curves dr_1 and dr_2, then is formed the osmotic equilibrium:

$$E = L_t \mid L_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

As we shall deduce further, it depends not only on the composition, but also on the ratio of the quantities of the original liquids L_s and L_u, on which isotonic curves they will get the same O.W.A.

In order to show this, we take n_1 quantities of L_s with the composition (4^a) and n_2 quantities of L_u with the composition (4^b).

We assume that from this arise, n_1' quantities of a liquid $L_{s'}$ with the composition:

$$x_1' X + y_1' Y + (1 - x_1' - y_1') W$$

and n_2' quantities of $L_{u'}$ with the composition:

$$x_2' X + z_2' Z + (1 - x_2' - z_2') W.$$

If we express that the total quantity of the diffusing substance W remains constant and that also the quantity of each of the not-diffusing substances X, Y and Z remains constant on each of the sides of the membrane, then we find the equations:

$$\left.\begin{array}{c} n_1' + n_2' = n_1 + n_2 \\ n_1' x_1' = n_1 x_1 \qquad n_1' y_1' = n_1 y_1 \qquad n_2' x_2' = n_2 x_2 \qquad n_2' z_2' = n_2 z_2 \end{array}\right\} \quad (7)$$

From this follows by elimination of n_1' and n_2':

$$\frac{x_1'}{y_1'} = \frac{x_1}{y_1} \qquad \frac{x_2'}{x_2} = \frac{z_2'}{z_2} \qquad 1 + \frac{n_2}{n_1} = \frac{x_1}{x_1'} + \frac{n_2}{n_1} \cdot \frac{x_2}{x_2'} \quad . \quad . \quad . \quad (8)$$

The first one of those equations expresses that the liquid $L_{s'}$ proceeds along the line Ws, the second one expresses that the liquid $L_{u'}$ proceeds along the line Wu; it appears from the third one that the composition depends also on the ratio $n_2 : n_1$.

The equations (8) are valid for each arbitrary moment of the diffusion; those three equations contain four unknowns. When the equilibrium takes place, then the variables x'_1, y'_1, x'_2 and z'_2 have to satisfy also an equation, which is deduced from (5) by giving in this an accent to each of the variables. Then we have four equations with four unknowns so that the composition of both the liquids after the diffusion is defined completely.

We imagine to be drawn in fig. 1 on the line su a point k, which divides this line into two parts, which are defined by:

$$sk : uk = n_2 : n_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We may imagine that this point k represents the complex of n_1 quantities of L_s and n_2 quantities of L_u.

During the diffusion the liquid $L_{s'}$ is situated anywhere in a point s' on the line st (between s and t), the liquid $L_{u'}$ anywhere in a point u' on the line uv (between u and v). We are able now to show that the conjugation-line $s'u'$ goes perpetually through the point k. Consequently this must also be the case with the line tv.

The above should be clear without more, if the liquids u' and s' belong to the same ternary system; here, however, we have two different ternary

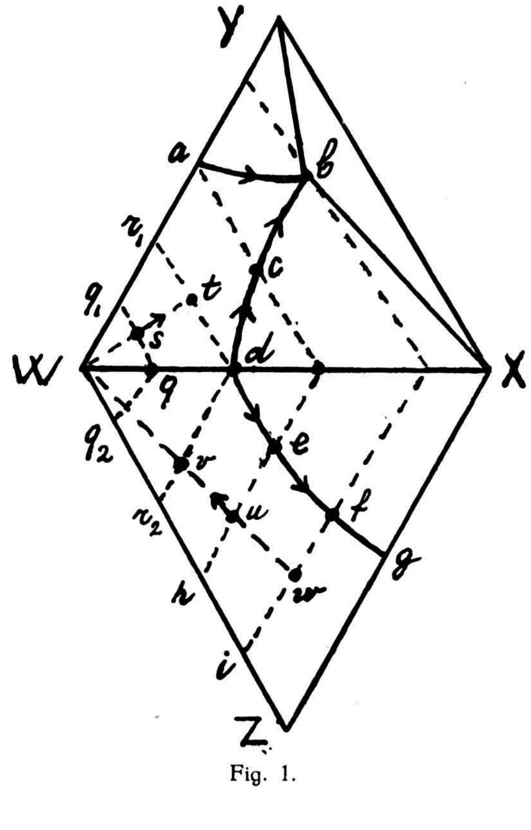

Fig. 1.

systems which form together a quaternary system. The liquids under consideration are situated in two of the four triangles, which limit the tetrahedron $WXYZ$, which should represent in space this quaternary equilibrium. Consequently the complex k is situated really in space within the tetrahedon and not in the plane of fig. 1, which represents only two side-planes of the tetrahedron, drawn in a same plane.

If, however, we consider fig. 1 as a perspective projection of the tetrahedon $WXYZ$, then follows from this at once the property above mentioned; we are able to deduce this still also in the following way.

From fig. 1 viz. follows that we may put:

$$Ws = \alpha x_1 \qquad Ws' = \alpha x_1' \qquad Wu = \beta x_2 \qquad Wu' = \beta x_2' \quad , \qquad (10)$$

in which α and β have definite values. If we take the line Wu as X-axis and the line Wt as Y-axis of a system of coördinates, then is:

$$\frac{X}{\beta x_2} + \frac{Y}{\alpha x_1} = 1 \qquad \text{the equation of the line } su$$

$$\frac{X}{\beta x_2'} + \frac{Y}{\alpha x_1'} = 1 \qquad \text{,, \quad ,, \quad ,, \quad ,, \quad ,, } s'u'$$

Calculating from this the X or the Y of the point of intersection k of those two lines, then we easily find:

$$sK : uK = \left(\frac{x_1}{x_1'} - 1\right) : \left(1 - \frac{x_2}{x_2'}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

With the aid of (7) we find from this the equation (9) so that the property above mentioned is proved.

In fig. 1, therefore, k shall be the point of intersection of the lines su and tv; the liquids s' and u', which occur during the diffusion, are situated, therefore, in such a way that the line $s'u'$ goes through the point k.

We now consider the osmotic system:

$$X + L_d \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

of fig 1. As L_d is the liquid, which is formed when the solid substance X takes a little water in, L_d has the same O.W.A. as the solid substance X. In a similar way and with the same way of representation as previously (compare f.i. Comm. VII) we find:

$$E = X + L_d \mid L\,(1 - dr_1 - dr_2) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

$$X \leftarrow\!\mid L\,(2 - Wdr_1 - Wdr_2) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

$$X \mid L\,(2 - dr_1\,YX - dr_2\,ZX) \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

Limiting ourselves to stable liquids (viz. only to the unsaturated and saturated liquids, excluding the supersaturated liquids) then (15) passes into:

$$X \mid L(2 - dr_1\, ab - dr_2\, Zg) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

(13) indicates that the liquid L, which is isotonic with the liquid L_d, has one freedom and is represented by points of the curves dr_1 and dr_2.

(14) means that the liquids from which water diffuses towards the solid substance X, have two freedoms and are represented by points of the regions Wdr_1 and Wdr_2.

(16) means that the liquids, which can be in osmotic contact with the solid substance X, without anything happening, have two freedoms and are represented by points of the region $dr_1\, a\, b$ or $dr_2\, Z\, g$.

We may express this also in the following way:

the O.W.A. of the solid substance X is equal to that of the liquids of curves dr_1 and dr_2, larger than that of the liquids of the regions Wdr_1 and Wdr_2 and smaller than that of the liquids of the regions $dr_1\, a\, b$ and $dr_2\, Zg$.

Let us take now the osmotic system:

$$Y + L_a \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which L_a (fig. 1) is the liquid, which arises, when the solid substance Y takes a little of the diffusing substance W. We now find:

$$E = Y + L_a \mid L(1 - ac - eh) \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$Y \leftarrow L(2 - Wdca - Wdeh) \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$Y \mid L(2 - acb - eh\, Zg) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This means: the O.W.A. of the solid substance Y is equal to that of the liquids of curves ac and eh, larger than that of the liquids of the regions $Wdca$ and $Wdeh$ and smaller than that of the liquids of the regions acb and $ehZg$.

Consequently here a series of liquids exists, which do not contain the substance Y (viz. of curve eh) and yet they have the same O.W.A. as the solid substance Y. Also there are now two liquids, saturated with the solid substance X, which have also the same O.W.A. as the solid substance Y. One of them (viz. liquid c) contains the substance Y, the other one (viz. liquid e), however, does not contain the substance Y.

In the osmotic system:

$$X + Y + L_b \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

L_b is the liquid which arises, when solid $X+Y$ takes a little water in. Limiting ourselves again to stable states, then we find:

$$E = X + Y + L_b \mid L\,(1 - fi) \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$X + Y \overset{|}{\leftarrow} L\,(2 - Wdba - Wdfi) \quad . \quad . \quad . \quad (23)$$

$$X + Y \mid L\,(2 - fi\,Zg) \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Consequently there is only one liquid, containing $X + Y$, viz. L_b, which has the same O.W.A. as the solid mixture $X + Y$; indeed there is still a series of liquids, viz. those of curve fi, which also have this same O.W.A. but those liquids do not contain the substance Y.

Also we find in the system $W + X + Y$ no liquids with a greater O.W.A. than those of the solid mixture $X + Y$; we find them in the region $fiZg$ of the system $W + X + Z$.

If we bring in osmotic contact L_c and L_u then nothing happens; both liquids are situated viz. on conjugated isotonic curves and have, therefore, the same O.W.A.

If we bring in osmotic contact L_c and L_v then, as the O.W.A. of L_c is greater than that of L_v, the inversion:

$$L_c \overset{|}{\leftarrow} L_v$$

shall occur; the saturated liquid L_c shall become unsaturated, therefore.

If we bring in osmotic contact L_c and L_w, then water shall diffuse from L_c towards L_w; consequently we have:

$$L_c \overset{|}{\rightarrow} L_w \,.$$

Consequently L_c shall pass into a liquid between c and b, with separation of the solid substance X.

If we bring in osmotic contact solid $X + Y$ with L_v, then, as the O.W.A. of the solid $X + Y$ is greater than that of liquid L_v, water shall diffuse from the liquid towards $X + Y$. Consequently we get the inversion:

$$X + Y \overset{|}{\leftarrow} L_v \,.$$

When a sufficient quantity of $X + Y$ is present, then at last is formed the osmotic equilibrium:

$$E = X + Y + L_b \mid L_w \,.$$

Both the systems contain one common component only.

We now take the osmotic equilibrium:

$$E = E_1 \mid E_2$$

in which the separate parts have only the diffusing substance W in common. We shall represent the phases of E_1 with the components $W + X + Y$ by points of triangle WXY (fig. 2); those of system E_2 with the components $W + Z + U$ by points of triangle WZU (fig. 3).

We assume, as is apparent from those two diagrams, that in the one system the components X and Y occur as solid phases, in the other system the component U. The arrows on the saturation-curves *ci*, *hi* and *em* indicate the direction in which the O.W.A. of the saturated solutions increases.

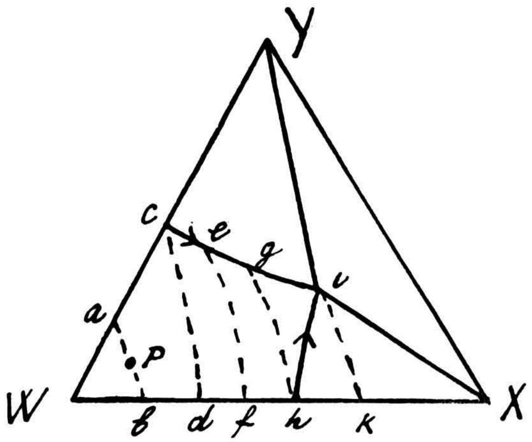

Fig. 2.

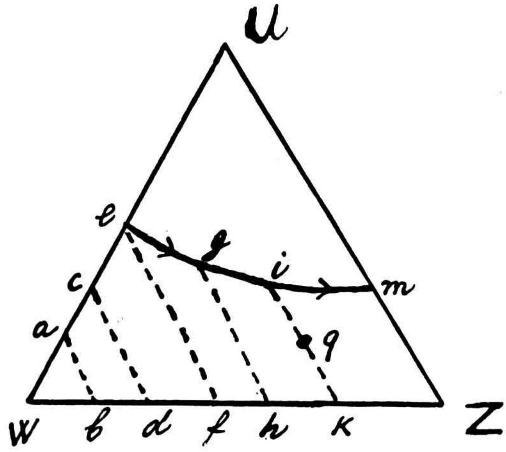

Fig. 3.

We now draw in fig. 2 an isotonic curve *ab*; now we are able to draw also in fig. 3 an isotonic curve *ab*, the liquids of which have the same O.W.A. as the liquids of curve *ab* in fig. 2. The curves *ab* of figs. 2 and 3, which we shall call for the sake of distinction $(ab)_2$ and $(ab)_3$ are, therefore, conjugated isotonic curves.

We now assume that the dotted curves, which are indicated in both figures by the same letters, represent also conjugated isotonic curves; f.i. $(cd)_2$ and $(cd)_3$; $(ef)_2$ and $(ef)_3$; etc.

For the osmotic equilibrium:

$$E = L_2 \mid L_3$$

in which L_2 represents a liquid of fig. 2 and L_3 a liquid of fig. 3, is true the equation for equilibrium:

$$\zeta_2 - x\frac{\partial \zeta_2}{\partial x} - y\frac{\partial \zeta_2}{\partial y} = \zeta_3 - z\frac{\partial \zeta_3}{\partial z} - u\frac{\partial \zeta_3}{\partial u} \quad \ldots \quad (25)$$

in which ζ_2 and ζ_3 represent the thermodynamical potentials of the liquids L_2 and L_3.

We now bring in osmotic contact liquid L_p [on curve $(a\,b)_2$] with liquid L_q [on curve $(i\,k)_3$]. As the O.W.A. of L_q is greater than that of L_p, water shall diffuse from L_p towards L_q. Consequently L_q moves along the line Wq starting from q towards W; L_p shifts along the line Wp further away from p. For this diffusion, which continues till both liquids reach conjugated isotonic curves, the same is true as is deduced above for fig. 1.

In the osmotic system:

$$Y + L\,(c)_2 \;\vdots\; L$$

$L(c)_2$ (fig. 2) is the liquid, which arises when a little water diffuses towards the solid substance Y. Limiting ourselves again to stable states, then follows:

$$E = Y + L\,(c)_2 \;\vdots\; L\,[1-(cd)_2-(cd)_3]$$

$$Y \overset{\vdots}{\leftarrow} L\,[2-(Wcd)_2-(Wcd)_3]$$

$$Y \;\vdots\; L\,[2-(cdhi)_2-(cdZme)_3]\,.$$

This means: the O.W.A. of the solid substance Y is equal to that of the liquids of curve $c\,d$ in figs. 2 and 3; greater than that of the liquids of the region $W c\,d$ in figs. 2 and 3; smaller than that of the liquids of the region $c\,d\,h\,i$ in fig. 2 and of the region $c\,d\,Z\,m\,e$ in fig. 3.

If we bring in osmotic contact the solid substance Y with liquid q (which contains the components $W + U + Z$) then nothing happens, therefore; if, however, we bring in osmotic contact solid Y with a liquid of curve $(a\,b)_3$ [which contains, therefore, also the components $W + U + Z$] then Y shall flow away totally or partly.

In the osmotic system:

$$X + L\,(h)_2 \;\vdots\; L$$

$L(h)_2$ (fig. 2) is the liquid which arises when the solid substance X takes a little water in.

We find from this:

$$E = X + L\,(h)_2 \;\vdots\; L\,[1-(hg)_2-(hg)_3]$$

$$X \overset{\vdots}{\leftarrow} L\,[2-(Whgc)_2-(Whge)_3]$$

$$X \;\vdots\; L\,[2-(hgi)_2-(hgmZ)_3].$$

From this appears a.o. that from all liquids of the region $Whgc$ in fig. 2 (consequently with the components $W+X+Y$) and from all liquids of the region $Whge$ in fig. 3 (consequently with the components $W+Z+U$) water will diffuse towards the solid substance X; the other liquids let X unchanged.

In similar way the reader may find also the liquids, which have either the same or smaller or greater O.W.A. than the solid substance U or the solid mixture $X+Y$.

If we bring in osmotic contact the solid substances X, Y or U or the solid mixture $X+Y$ with a liquid L, which contains the components $W+X+Y$ (fig. 2) or the components $W+Z+U$ (fig. 3) then we may distinguish several cases.

1. L is situated within the region Wcd of fig. 2 or 3.
   X, Y, U and $X+Y$ flow away totally or partly.
2. L is situated within the region $cdfe$ of fig. 2 or 3.
   X, U and $X+Y$ flow away totally or partly; Y remains unchanged.
3. L is situated within the region $efhg$ of fig. 2 or 3.
   X and $X+Y$ flow away totally or partly; Y and U remain unchanged.
4. L is situated within the region hgi of fig. 2 or within the region $hgik$ of fig. 3.
   $X+Y$ flows away totally or partly; X, Y and U remain unchanged.
5. L is situated within the region $ikZm$ of fig. 3.
   X, Y, U and $X+Y$ remain unchanged.

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