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

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Systems in which a substance different to water diffuses through the membrane.

Although the preceding considerations are valid generally, also when substance different to water is diffusing through the membrane, yet we shall consider a single case more in detail. Firstly we take the osmotic equilibrium

$$E = L_1 \,\vdots\, L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

of two liquids; we shall represent the composition of L_1 by $x_1X + y_1Y \ldots$ $\ldots + (1-x_1-y_1 \ldots.)\ W$, that of L_2 by substituting the index 1 by 2. If water (W) is the diffusing substance, then, when δn quantities of water diffuse from L_2 towards L_1, the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_W \,.\, \delta n \text{ in which } (\varphi_1)_W = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right)_1,$$

that of L_2 decreases with:

$$(\varphi_2)_W \,.\, \delta n \text{ in which } (\varphi_2)_W = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right)_2$$

and that of the total system increases, therefore, with:

$$[(\varphi_1)_W - (\varphi_2)_W] \,.\, \delta n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the component X is the diffusing substance, then, when δn quantities of X diffuse from L_2 towards L_1, the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_X \,.\, \delta n \text{ in which } (\varphi_1)_X = \left[\zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right]_1$$

that of L_2 decreases with:

$$(\varphi_2)_X \,.\, \delta n \text{ in which } (\varphi_2)_X = \left[\zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right]_2,$$

so that the thermodynamical potential of the total system increases with:

$$[(\varphi_1)_X - (\varphi_2)_X] \,.\, \delta n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If other components diffuse, corresponding equations are valid then, of course.

Previously we have seen that (2) defines in which direction the water diffuses in system (1); viz. the water goes towards that liquid which has the smallest φ. For that reason we have said that $(\varphi_1)_W$ and $(\varphi_2)_W$ define the osmotic water-attraction ($O.W.A.$) of the liquids L_1 and L_2 and that the $O.W.A.$ increases with decreasing φ. The same is also true for the osmose of the substance X.

If viz. $(\varphi_1)_X = (\varphi_2)_X$ then (3) is zero for all values of δn; consequently system (1) is in osmotic equilibrium with respect to the substance X; we may say, therefore, that the $O.X.A.$ (osmotic X-attraction) of both liquids is equal.

If $(\varphi_1)_X > (\varphi_2)_X$ then, as the thermodynamical potential of the total system can become only smaller, δn in (3) must be negative; consequently X diffuses from L_1 towards L_2. We may say, therefore, that the $O.X.A.$ of liquid L_2 is greater than that of L_1.

If $(\varphi_1)_X < (\varphi_2)_X$ then in (3) δn must be taken positive; consequently X diffuses from L_2 towards L_1. Now we may say, therefore, that the $O.X.A.$ of liquid L_1 is greater than that of L_2.

Consequently, as the substance X diffuses towards that liquid, which has the smallest φ, we may say, therefore, that φ defines the $O.X.A.$ of the liquid and that the $O.X.A.$ of a liquid increases with decreasing φ.

If in the osmotic equilibrium:

$$E = L \,\vdots\, L_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

in which L and L_1 are two ternary substances, the component Y is the diffusing substance, then must be satisfied:

$$\zeta - x\frac{\partial\zeta}{\partial x} + (1-y)\frac{\partial\zeta}{\partial y} = \left[\zeta - x\frac{\partial\zeta}{\partial x} + (1-y)\frac{\partial\zeta}{\partial y}\right]_1 \quad . \; . \; . \quad (5)$$

If we take in (4) a definite liquid for L_1 f.i. L_p, represented in fig. 1 by point p, then the second part of (5) has a definite value. The liquids L, which are isotonic with L_p with respect to the substance Y, are represented, therefore, by a curve $p_1\,p\,p_2$ going through the point p. Consequently this curve is an isotonic curve with respect to the diffusing substance Y; therefore, all liquids of those curves have the same $O.Y.A.$ (osmotic Y-attraction). We shall call the isotonic curves with respect to the substance W the „isotonic W-curves" and those with respect to the substance Y the „isotonic Y-curves".

If we take in (4) for L_1 the liquid L_q, represented by point q (fig. 1), then all liquids which are isotonic with L_q with respect to Y, are represented by a curve $q_1\,q\,q_2$. All liquids of this curve have the same $O.Y.A.$ therefore.

The same is true for the isotonic Y-curves, which go through other points f.i. through r or s.

Consequently all liquids of curve $p_1\,p\,p_2$ are isotonic with respect to the substance Y; the same is true for all liquids of curve $q_1\,q\,q_2$, etc. Liquids of different curves are not isotonic, however, f.i. liquid p not with q or with r_1 or with s_2 etc.

In Communication II we have deduced several properties of the isotonic W-curves; they are true also for the isotonic Y-curves. Consequently we have:

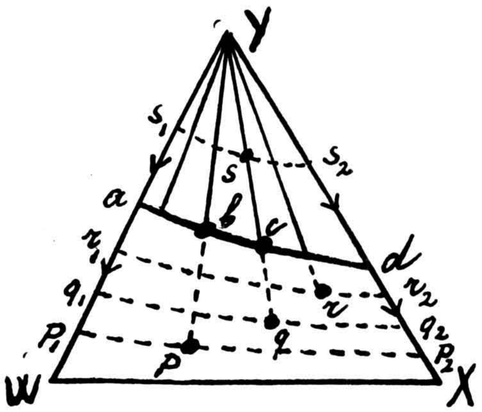

Fig. 1.

1. Each isotonic Y-curve has two ends; the one is situated on the side WY, the other on the side XY of the triangle.

2. Each straight line, drawn through the point Y, intersects the isotonic Y-curve in one point only.

3. Two different isotonic curves never can intersect or touch one another.

4. The isotonic Y-curves are straight lines in the vicinity of the point Y.

5. The $O.Y.A.$ is equal in all liquids of an isotonic Y-curve; it is greater, however, the further this curve is remoted from point Y.

We have deduced the properties of the isotonic W-curves in Communication II with the aid of the ζ-surface; in exactly the same way follow the properties of the isotonic Y-curves, mentioned above. Of course they may be deduced also in another way. The $O.Y.A.$ of a liquid L_q is viz. defined by:

$$\varphi = \left[\zeta - x\frac{\partial\zeta}{\partial x} + (1-y)\frac{\partial\zeta}{\partial y}\right]_q \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The $O.Y.A.$ of a liquid L'_q, the composition of which differs infinitely little from that of L_q is, therefore

$$\varphi' = \varphi + \triangle\varphi = \varphi + \frac{\partial\varphi}{\partial x}\triangle x + \frac{\partial\varphi}{\partial y}\triangle y \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or:

$$\triangle\varphi = [-rx + (1-y)\,s]_q\,\triangle x + [-sx + (1-y)\,t]_q\,\triangle y \quad . \quad . \quad (8)$$

Of all liquids L'_q which differ infinitely little from L_q we now take that liquid which arises from L_q by solution of a little Y. If δn quantities of Y dissolve in one quantity of L_q, then we have:

$$\triangle x = -\frac{x\,.\,\delta n}{1+\delta n} = -x\,.\,\partial n \qquad \triangle y = \frac{(1-y)\,.\,\delta n}{1+\delta n} = (1-y)\,.\,\delta n \quad (9)$$

so that (8) passes into:

$$\triangle\varphi = [x^2 r - 2x(1-y)\,s + (1-y)^2\,t]\,.\,\delta n \quad . \quad . \quad . \quad . \quad (10)$$

The stability requires that the coefficient of δn is positive; consequently $\triangle\varphi$ is also positive for positive values of δn. With solution of Y in the liquid L_q the φ of this liquid increases therefore and its $O.Y.A.$ decreases.

In a similar way we may deduce the general rule:

if a little of a substance dissolves in a liquid, then its osmotic attraction with respect to this substance becomes smaller.

As is already said above, this rule is true, however, only for stable liquids. Later we shall see in systems, in which dimixtion into two or more liquids can occur, that this rule is valid no more for liquids, which are unstable, in itself.

Hence follows, in accordance with the rule, mentioned above sub 5, that the O.Y.A. of liquids of curve $q_1 q q_2$ is greater than that of curve $r_1 r r_2$ and smaller than that of curve $p_1 p p_2$. Consequently the O.Y.A. increases in the direction of the arrows, drawn in fig. 1 on the sides YW and YX.

We now assume that the diffusing substance Y can occur as solid phase; its saturation-curve is represented in fig. 1 bij $a b c d$. Consequently this is defined by

$$\zeta - x\frac{\partial \zeta}{\partial x} + (1-y)\frac{\partial \zeta}{\partial y} = \zeta_y \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

in which ζ_y represents the thermodynamical potential of the solid substance Y. As the O.Y.A. of an arbitrary liquid L_q is defined by (6), it follows from (11) that all liquids of curve $a b c d$ have the same O.Y.A. This is in accordance with the rule, deduced in Communication II.

All liquids, which are saturated with a solid substance, are isotonic with respect to this substance.

The saturation-curve $a\ b\ c\ d$ in fig. 1 is an isotonic Y-curve therefore; the isotonic Y-curves, in the vicinity of curve $a\ b\ c\ d$, must have, therefore, a corresponding form.

Consequently the isotonic curves can have several forms, just as the saturation-curves. Let us take f.i. the saturation-curve $w c d v$ of the solid substance Y in fig. 3 Comm. III. We can represent the equilibria which occur at 4°5 in the system water + alcohol + nitril of succinic acid [1]) schematically by this figure, if W is water, X alcohol and Y the nitril of succinic acid. The isotonic curves of nitril of succinic acid will have in the vicinity of curve $w c d v$ a similar form with two points of inflexion.

Above we have seen that the O.Y.A. of the liquids of an isotonic Y-curve is greater, the further those curves are remoted from the point Y. We now see from fig. 1 that an unsaturated solution has a greater O.Y.A. and a supersaturated solution has a smaller O.Y.A. than a solution saturated with Y. This is in accordance with the meaning of: saturated, unsaturated and supersaturated solution.

We now take the osmotic system:

$$L_p \overset{|}{\underset{|}{\leftarrow}} L_r \quad \text{fig. 1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

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[1]) F. A. H. SCHREINEMAKERS, Zeitschr. f. Phys. Chem. **27**, 144 (1898).

in which, as according to fig. 1, L_p has a greater $O.Y.A.$ than L_r, the substance Y shall diffuse in the direction of the arrow. Consequently in fig. 1 L_p shifts from point p along the line pY towards Y and L_r from point r along the line Yr away from Y. The diffusion of the substance Y continues, till both liquids reach a same isotonic Y-curve f.i. curve $q_1 q q_2$.

In the osmotic system:

$$L_p \mathrel{\overset{|}{\underset{|}{\leftarrow}}} Y + L_c \quad \text{fig. 1} \quad \ldots\ldots\ldots \quad (13)$$

the substance Y diffuses in the direction of the arrow, as follows from fig. 1. Now is formed one of the osmotic equilibria:

$$E = L_b \mid Y + L_c \; \ldots \; (14^a) \qquad E = L'_p \mid L'_c \; \ldots\ldots \; (14^b)$$

If viz. a sufficient quantity of solid Y is present, then L_p of (13) passes into the saturated liquid L_b of (14^a); if in (13) there is too little solid Y, then arise the two unsaturated liquids of (14^b); if both liquids are situated f.i. on the isotonic curve $r_1 r r_2$ then L'_p is represented by the point of intersection of this curve with the line pY and L'_c by the point of intersection of this curve with the line Yc.

Consequently the disappearance of the solid substance Y from (13) when passing into (14^b) is here a consequence of the diffusion of the substance Y itself and not, as we have seen several times in the previous communications, a consequence of diffusion of water.

If we assume that the solid substance Y forms a hydrate H, then we may represent the saturation-curve of H by curve $wcdv$ of fig. 1 Communication IV. The dotted curves of this figure are isotonic W-curves. We have called in this Communication IV point w the finishing-point of this curve rich in water and point v the point poor in water. Then we have found the rule:

The $O.W.A.$ of a liquid of a saturation-curve of a hydrate is greater, the further this liquid is remoted from the finishing-point of this curve rich in water.

Consequently the $O.W.A.$ of the liquids must increase in the direction of the arrows along this curve. We may call point w the finishing-point of curve $wcdv$ poor in Y and point v the point rich in Y. Then we find the rule:

the $O.Y.A.$ of the liquids of a saturation-curve of a hydrate of Y is greater according this liquid being situated further from the finishing-point of this curve rich in Y.

Consequently we have to give the opposite direction to the arrows in fig. 1. Comm. IV.

Of course the isotonic Y-curves have quite another proceeding than the isotonic W-curves, drawn in the figure; we have to imagine the points m n and o, which we shall call now m_1 n_1 and o_1, to be situated on the side YX. Then point o_1 is situated the closest to Y, point m_1 the farthest from Y. Drawing this curve we must bear in mind the rule, already previously deduced:

an isotonic curve and a saturation-curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle; if one of those curves touches the one leg of the angle, then the other curve touches the other leg.

In point c of fig. 1 Comm. IV the conjugation-angle is HcY; the saturation-curve is situated out of this angle, consequently within the supplement-angle; the isotonic Y-curve going through point c must, therefore, be situated also within this angle. If we imagine to be drawn from Y to curve $w\,c\,d\,v$ a tangent, which touches this curve in point r (not drawn) then HrY is the conjugation-angle. As the saturation-curve touches the leg rY, the isotonic curve must touch, therefore, the leg rH.

In the osmotic system:

$$L_b \overset{|}{\underset{|}{\leftarrow}} L_d \quad \text{fig. 1 Comm. IV} \;.\;.\;.\;.\;.\;.\; (15)$$

L_b has a greater $O.Y.A.$ than L_d; consequently the substance Y diffuses in the direction of the arrow in (15). Therefore liquid L_b shall separate solid H and pass into another liquid of the saturation-curve, f. i. into L_c. Then liquid L_d passes into an unsaturated liquid L'_d, which is represented by the point of intersection of the line Yd with the isotonic Y-curve $n'c\,n_1$ going through point c. Consequently system (15) passes into the osmotic equilibrium:

$$E = H + L_c \;\vdots\; L'_d \quad \text{fig. 1 Comm. IV} \;.\;.\;.\; (16)$$

The complex of the liquids L_b and L_d of (15) is represented by a point s on the line $b\,d$, not-drawn in the figure. As the quantities of the substances in the total system do not change by the diffusion, the complex of system (16) must be represented also by this point s. The complex $H + L_c$ is represented by a point on the line Hc, which we shall call c'; liquid L'_d is situated in the point of intersection d' (not-drawn) of line Yd and the isotonic Y-curve going through c. Consequently the line $c'd'$ must go through the point s.

In the osmotic system:

$$L_b \overset{|}{\underset{|}{\leftarrow}} L_f \quad \text{fig. 1 Comm. IV} \;.\;.\;.\;.\;.\;.\; (17)$$

the substance Y diffuses from L_f towards L_b, as L_b has a greater $O.Y.A.$ than L_f. Both liquids now pass with separation of the hydrate H into a liquid of curve $w\,c\,d\,v$ situated between b and f. If the complex of the two liquids in (17) is situated f.i. on the line Hd, then (17) passes into:

$$E = H + L_d \;\vdots\; H + L_d \quad \text{fig. 1 Comm. IV} \;.\;.\;.\; (18)$$

The directly visible result of the diffusion in system (17) is, therefore, that the hydrate H is separated on both sides of the membrane; in system (15) this hydrate is separated at one side of the membrane only.

All we have deduced above, if H is hydrate of Y, viz. a compound of Y and W, is true also when Y forms a binary compound with the component X; then the point H is situated on the side YX of this figure.

If Y forms with water and X a ternary compound D, then we can represent the saturation-curve of D by curve $w\,b\,v\,d\,w$ of fig. 2 Communication IV; the dotted curves in this figure are the isotonic W-curves. The line WD intersects the saturation-curve in the points w and v; they divide this curve into two branches; we have called w the finishing-point of those branches rich in water and v the point poor in water. Previously we have deduced:

the $O.W.A.$ of a liquid of this saturation-curve is greater, the further it is remoted from the finishing-point rich in water.

Consequently the $O.W.A.$ increases along both branches in the direction of the arrows.

We now imagine in this figure to be drawn the line YD, which intersects the saturation-curve in two points; these points of intersection divide this curve into two branches. We call the point of intersection, which is situated the closest to Y the finishing-point of those branches, rich in Y, the other the point poor in Y. We now find the rule:

the $O.Y.A.$ of a liquid of the saturation-curve is greater, the further it is remoted from the finishing-point rich in Y.

We may consider fig. 2 of this communication as special case of fig. 2 in Comm. IV; here point D is situated on the side WX and is, therefore, a hydrate of the substance X. The line YD divides the saturation-curve $a\,d\,g$ into the two branches $a\,d$ and $g\,d$; point d is the finishing-point rich in Y. Consequently the $O.Y.A.$ must increase from d towards a and from d towards g; therefore, in the direction of the arrows. The dotted curves are isotonic Y-curves; consequently b and f have the same $O.Y.A.$, they are isotonic, therefore, with respect to the substance Y; the same is true for the

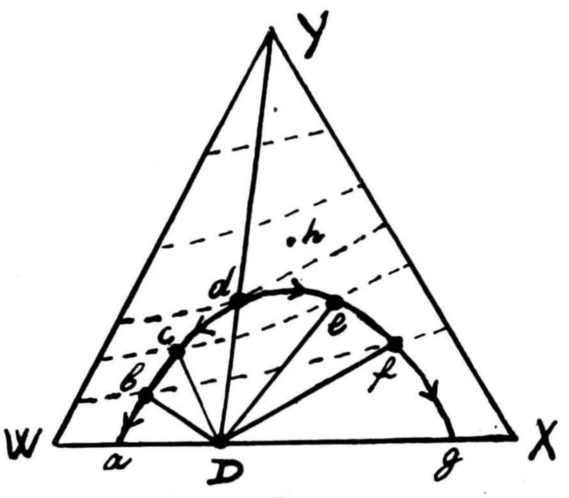

Fig. 2.

liquids c and e. The isotonic Y-curve, going through point d, touches the saturation-curve in this point d. The conjugation-angle in point c is DcY; the saturation-curve and the isotonic Y-curve are situated in the vicinity of c within this conjugation-angle; this is also the case in the points b, e and f. If the saturation-curve has such a form, that we may draw from Y a line, which touches this curve in a point r, then the isotonic Y-curve, going through r, must touch the line rD.

In the osmotic system:

$$L_h \overset{|}{\underset{|}{\rightarrow}} L_f \quad \text{fig. 2} \quad \dots\dots\dots \quad (19)$$

L_f has a greater $O.Y.A.$ than L_h; consequently, as is indicated in (19) by the arrow, the substance Y diffuses from L_h towards L_f. It now depends on the ratio of the two liquids in (19), which osmotic equilibrium will be formed at last; f. i. the equilibrium:

$$E = D + L_e \,\big|\, L'_f \quad \text{fig. 2} \quad \dots\dots\dots \quad (20)$$

may arise; then L'_f is the liquid, represented by the point of intersection of the line Yf with the isotonic Y-curve, going through point e. Therefore, a result of the diffusion of the substance Y, visible at the moment, is, that a hydrate of the substance X is separated at one side of the membrane; at first sight the substance X might seem to be diffusing, instead of the substance Y.

As special case of fig. 2 we may assume that point D coincides with W or X. If D coincides with X, then of curve adg only the branch ad remains, point d of which is situated now on the side XY; the $O.Y.A.$ then also increases in the direction of the arrows, viz. from d towards a. Then, however, the isotonic Y-curve going through point d, touches no more the saturation-curve in d. If D coincides with W then of adg only remains the branch dg, point d of which is situated now on the side WY, dg now represents the solutions, which are in equilibrium with ice. Then the $O.Y.A.$ of those solutions, saturated with ice, increases also in the direction of the arrows, viz. from d towards g.

We may easily summarise the rules deduced in this and previous communications for the change of the osmotic attraction of the liquids of a saturation-curve. We take the saturation-curve of an arbitrary substance V (component or compound); we call N the diffusing substance. The line NV intersects the saturation-curve of V in one or two points; in both cases one of the points of intersection is situated between V and N; we call this the „point rich in N" of the saturation-curve. We now can say:

the $O.N.A.$ (osmotic N-attraction) of a liquid of a saturation-curve is greater, the more this liquid is situated further from the point of this curve, rich in N.

In the special case, that the solid substance, with which the liquids of the saturation-curve are in equilibrium, is the diffusing substance itself, the line NV does not exist and consequently there is no point on the saturation-curve rich in N. Then the former rule passes into:

all liquids of the saturation-curve of a substance N have the same $O.N.A.$

If we apply this rule to the saturation-curve $w\,v$ of the substance Y n the figs. 1, 2 and 3 of Communication III, then we find:

the $O.W.A.$ increases along curve $w\,v$ from w towards v,
„ $O.X.A.$ „ „ „ „ „ v „ w,
„ $O.Y.A.$ is the same for all liquids of curve $w\,v$.

For the saturation-curve $w\,c\,d\,v$ of the hydrate H in fig. 1 of Communication IV follows:

the $O.W.A.$ increases along curve $w\,v$ from w towards v,
„ $O.Y.A.$ „ „ „ „ „ v „ w,
„ $O.X.A.$ „ „ „ „ „ s „ w and from s towards v, if s is the point of intersection of this curve with the line HX.

For the saturation-curve $a\,d\,g$ of the hydrate D in fig. 2 of this communication we find:

the $O.W.A.$ increases along this curve from a towards g.
„ $O.X.A.$ „ „ „ „ „ g „ a.
„ $O.Y.A.$ „ „ „ „ „ d „ a and from d towards g.

In the figs. 1—4 of Communication V the arrows indicate the direction in which the $O.W.A.$ increases along the different saturation-curves; of course this is otherwise for the $O.X.A.$ and $O.Y.A.$ of those liquids.

We find for fig. 1 of Communication V:

the $O.Y.A.$ is constant along curve $a\,c$ and increases on curve $c\,b$ from c towards b.

If we imagine viz. curve $b\,c$ to be prolongated up to a point s on the side $X\,Y$, then s is the point of this curve rich in Y; the $O.Y.A.$, therefore, must increase along this curve from s towards b, consequently also from c towards b.

For fig. 2 of Communication V we find:

the $O.Y.A.$ decreases from a towards d, rests constant d to c and increases c to b.

For figs. 3 and 4 of Communication V follows:

the $O.Y.A.$ is constant from a to c and increases along the curves $c\,d$ and $d\,b$ from c to b.

We now may draw easily in those diagrams schematically the isotonic Y-curves; in the vicinity of the side WX their shape comes near to straight lines; in the vicinity of the saturation-curve of Y they get corresponding forms as this saturation-curve.

(To be continued.)