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

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

In fig. 1 ab represents the saturation-curve of a hydrate H and bc that of the solid substance Y. For the present we let out of consideration the saturation-curve of the solid substance X, represented in the figure by curve de, and, therefore, we imagine this disappeared out of the figure.

If we take the component Y as diffusing substance, then follows, as we have seen in the previous communication, that the $O.Y.A.$ (osmotic Y-attraction) of the liquids of the saturation-curve ab increases in the direction of the arrows, viz. from b towards a. As bc is the saturation-curve of solid Y, all liquids of this curve have the same $O.Y.A.$ The dotted curves represent isotonic Y-curves; in the previous communication we have seen that in the vicinity of curve bc these curves have a similar form as this curve, and that the $O.Y.A.$ of their liquids becomes larger, the farther these curves are situated away from the point Y.

Let us firstly consider the osmotic system

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

in which, as L_r has a greater $O.Y.A.$ than L_p, the substance Y diffuses in the direction, indicated by the arrow. Consequently L_p moves in the diagram along the line Yp away from the point Y and L_r along the line rY towards the point Y. This diffusion continues till both liquids reach the same isotonic curve f. i. curve lm. Then liquid L_r comes in point s and liquid Lp in point t; therefore the osmotic system (1) passes into the osmotic equilibrium:

$$E = L_s \;\vert\; L_t \; .$$

If we imagine the complex of the liquids of system (1) to be represented by a point K, then of course the line st must go through this point K.

We now bring into osmotic contact the solid substance Y with a liquid of the field $buXc$, f. i. with the liquid L_t; then we have the osmotic system

$$Y \overset{|}{\underset{|}{\rightarrow}} L_t \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Although at one of the sides of the membrane the substance Y is present not in solution, but in solid state, yet we will assume that it can diffuse. In previous communications viz. we have discussed already that we may also imagine the membrane as a liquid mass in which solid Y is soluble.

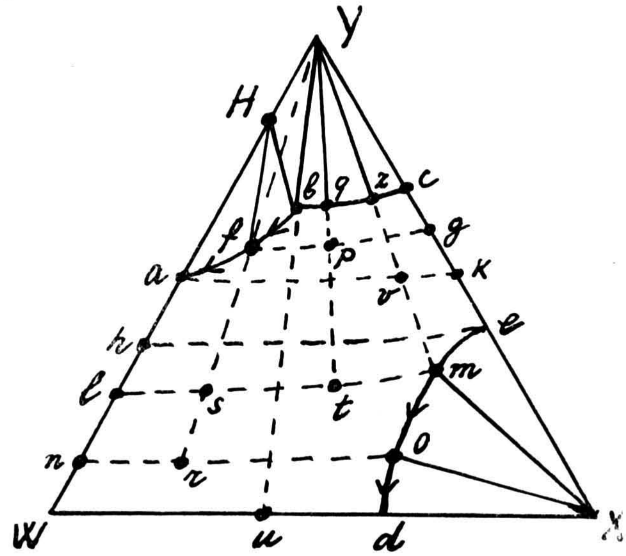

Fig. 1.

If now in (2) Y diffuses from left to right, then L_t traces the line tY in the direction towards Y. If a sufficient quantity of solid Y is present, then the diffusion continues till L_t comes in the point q of the saturation-curve bc, then system (2) passes into the osmotic equilibrium:

$$E = Y \mid L_q \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This is in accordance with the deduced previously that the $O.Y.A.$ of the solid substance Y is equal to that of the liquids of the saturation-curve bc, but that all liquids, which are unsaturated with respect to solid Y, have a greater $O.Y.A.$ Consequently in system (2) the substance Y must diffuse towards the liquid so long till this passes into the saturated solution L_q. In this special case we should obtain the same result, if we should take away the membrane in system (2) and we should bring Y in direct contact with the liquid L_t.

We now bring in osmotic contact solid Y with a liquid of the region $buWa$ (fig. 1) f.i. with the liquid L_r; then we have the osmotic system:

$$Y \xrightarrow{\mid} L_r \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

in which, just as in system (2) the $O.Y.A.$ of the liquid is greater than that of the solid substance Y. As the line rY intersects the sector Hab, system (4) shall pass, if a sufficient quantity of solid Y is present, into the osmotic equilibrium:

$$E = Y \mid H + L_b \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Every liquid of the field $buWa$, in osmotic contact with solid Y, passes, therefore, with separation of the hydrate H into the solution L_b.

Let us consider now the osmotic system:

$$H \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which L is an arbitrary liquid. One can imagine two cases now. If a little Y diffuses from the liquid to the solid hydrate, then is formed at the left side $H + Y$; if, however, a little Y diffuses from the hydrate to the liquid L, then is formed at the left side a little of the solution L_a, which contains water $+ Y$ only. Consequently system (6) passes, according to Y diffusing either towards left or right, into one of the systems:

$$H + Y \mid L \quad . \quad . \quad . \quad (7^a) \qquad\qquad H + L_a \mid L \quad . \quad . \quad . \quad (7^b)$$

The $O.Y.A.$ of solid $H + Y$ is equal now to that of solid Y, therefore, equal to that of the liquids of curve bc. The $O.Y.A.$ of $H + L_a$ is equal to that of L_a, therefore, equal to that of the liquids of the isotonic curve ak. Consequently we can distinguish two cases, according to the composition of liquid L in (6).

1. The liquid is situated in the field $abck$ (fig. 1).

If we take f.i. the liquid L_p then we have the osmotic system:

$$H \mid L_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If a little Y diffuses from the liquid towards the left, then an osmotic system (7^a) arises. As, however, L_p has a greater $O.Y.A.$ than $H + Y$ (which is equal to that of the liquids of curve bc), Y wil diffuse again back to the liquid. Consequently not a system (7^a) will be formed.

If a little Y diffuses from the hydrate towards the liquid, then a system (7^b) arises. L_p has a smaller $O.Y.A.$ than the liquids of the isotonic curve ak, consequently smaller also than liquid L_a. Therefore, this liquid L_a will remove again Y from L_p and will pass by this into solid H. Consequently also not a system (7^b) can be formed.

As system (8) can pass neither into a system (7^a) nor into a system (7^b), it follows, therefore:

the hydrate H can be in osmotic contact with all liquids of the field $abck$, without diffusion occurring.

2. The liquid is situated in the field $akXW$ (fig. 1).

If we take the liquids L_r and L_t then we have the osmotic systems:

$$H \mid L_r \quad . \quad . \quad . \quad (9^a) \qquad\qquad H \mid L_t \quad . \quad . \quad . \quad (9^b)$$

If a little Y diffuses from the liquid towards the left, then a system (7^a) arises; as, however, L_r and L_t have a greater $O.Y.A.$ than $H + Y$, Y shall diffuse away back to the liquid. Consequently no system (7^a) will be formed.

If, however, a little Y diffuses from the hydrate H towards the liquid, then a equilibrium (7^b) is formed. L_r and L_t, however, have a greater $O.Y.A.$ than the liquids of the isotonic curve ak and, therefore, a greater $O.Y.A.$ than the liquid L_a in (7^b). Consequently L_r and L_t will remove Y from L_a, but L_a will keep its composition by solution of this hydrate, as long as a sufficient quantity of H is present. If a sufficient quantity of solid H is present, then the diffusion continues till the liquids L_r and L_t have reached the isotonic curve ak. The systems (9^a) and (9^b) then pass into the osmotic equilibria:

$$E = H + L_a \mid L_r' \quad . \quad . \quad . \quad (10^a) \qquad E = H + L_a \mid L_t' \quad . \quad . \quad . \quad (10^b)$$

Herein L_r' and L_t' are the liquids which are represented by the points of intersection of the lines rY and tY with the isotonic curve ak.

If in the systems (9^a) and (9^b) no sufficient quantity of solid H is present, so that it has disappeared already before L_r and L_t have reached the isotonic curve ak, then L_a passes into an unsaturated solution; consequently in fig. 1 it is displaced starting from point a in the direction towards W. The diffusion of the substance Y stops when the liquids come on the same isotonic curve; if this is the case f. i. on curve he, then (9^a) and (9^b) pass into:

$$E = L_h \mid L_r'' \quad . \quad . \quad . \quad (11^a) \qquad E = L_h \mid L_t'' \quad . \quad . \quad . \quad (11^b)$$

in which L_r'' and L_t'' are liquids which are represented by the points of intersection of the lines rY and tY with the isotonic curve he.

We can summarise the previous results in the following way:

If we bring in osmotic contact the solid hydrate H (fig. 1):

a. with a liquid of the isotonic curve ak then there is osmotic equilibrium;

b. with a liquid of the field $akcb$ then nothing happens;

c. with a liquid of the field $akXW$ then the hydrate will flow away totally or partly.

If we assume that also the component X occurs as solid substance, then we can imagine the saturation-curve of X to be represented in fig. 1 by curve de. As follows from our previous communications, the $O.Y.A.$ of the liquids of this curve increases in the direction of the arrows, viz. from e towards d. We now consider the osmotic systems:

$$Y \xrightarrow{|} L_d + X \quad . \quad . \quad . \quad (12^a) \qquad H \xrightarrow{|} L_d + X \quad . \quad . \quad . \quad (12^b)$$

in which, therefore, L_d is a binary liquid, which contains the components water $+X$ and is saturated with solid X. We imagine the complex $L_d + X$ to be represented by the point of intersection m_1 of the line Ym and the side WX, which is not drawn. As the $O.Y.A.$ of L_d is greater than that of solid Y and of solid H, the substance Y will diffuse in (12^a) and (12^b) in the direction of the arrow.

The complex $L_d + X$ moves, therefore, by taking in Y, starting from m_1 towards point Y. Consequently liquid L_d firstly traces curve dm and afterwards the line mY. If a sufficient quantity of solid Y and H is present, then (12^a) and (12^b) pass into the osmotic equilibria:

$$E = Y \mid L_z \quad . \quad . \quad . \quad (13^a) \qquad\qquad E = H + L_a \mid L_v \quad . \quad . \quad . \quad (13^b)$$

One of the visible results of the diffusion Y is, therefore, the disappearance of the solid substance X. In (13^a) is formed the liquid L_z, which can be in equilibrium with solid Y, in (13^b) the unsaturated solution L_v, which is situated on the isotonic curve ak.

The conversion of (12^a) into (13^a) would take place also, if we take away the membrane; if, however, we take away the membrane in (12^b), then it is clear that (13^b) can not be formed.

In the osmotic system:

$$water \leftarrow\!\mid L_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the substance Y will diffuse from each liquid L_v towards the water. Then the water forms a binary liquid, which moves along the side WY in the direction towards Y. This diffusion continues till both liquids reach the same isotonic curve; if this is f.i. curve no, then (14) passes into the osmotic equilibrium:

$$E = L_n \mid X + L_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The visible result of the diffusion of the substance Y is, therefore, the separation of solid X from a liquid, originally unsaturated; this separation begins, as soon as the liquid L_v has reached the point m of the saturation-curve de.

We now consider the osmotic system:

$$X \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which L is an arbitrary liquid. If a little Y diffuses from the liquid towards the left, then is formed there a little of the liquid L_e (fig. 1); then system (16) passes into:

$$X + L_e \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The $O.Y.A.$ of the solid substance X is equal, therefore, to that of the liquid L_e and consequently equal also to the $O.Y.A.$ of the liquids of the isotonic curve eh. Therefore, all liquids of the region $ehWd$ have a greater $O.Y.A.$ and all liquids of the region $ehabc$ have a smaller $O.Y.A.$ than the solid substance X.

Hence follows:

If we bring in osmotic contact the solid substance X (fig. 1):

a. with a liquid of the isotonic curve *eh* then there is osmotic equilibrium;

b. with a liquid of the field *ehWd*, then nothing happens; the osmotic system remains unchanged, therefore;

c. with a liquid of the field *ehabc* then the solid substance X will flow away totally or partly.

The osmotic systems:

$$X \mid water \quad X \mid L \quad X \mid L_r \quad X \mid L_u \quad X \mid L_t \quad X \mid X + L_m \quad . \quad (18)$$

etc., the liquids of which are situated within the field *ehWd*, remain unchanged, therefore, without diffusion occurring. In the osmotic systems:

$$\left.\begin{array}{lll} X \overset{\mid}{\leftarrow} L_a & X \overset{\mid}{\leftarrow} H + L_f & X \overset{\mid}{\leftarrow} H + Y + L_b \\ X \overset{\mid}{\leftarrow} Y + L_q & X \overset{\mid}{\leftarrow} L_p & X \overset{\mid}{\leftarrow} L_g \end{array}\right\} \quad . \quad . \quad (19)$$

etc., the liquids of which are situated within the field *ehabc*, the substance Y diffuses in the direction of the arrows. If a sufficient quantity of solid X is present, then the equilibrium $X + L_e$ is formed at the left side of the membrane; at the other side of the membrane is formed a liquid, which is represented by a point of the isotonic curve *e h*. If too little solid X is present then is formed at the left side a solution, represented by a point between *e* and *c*.

The result of the diffusion is dependent on the ratio of the quantities of the different phases; if we take f.i. the osmotic system, mentioned already in (19):

$$X \overset{\mid}{\leftarrow} Y + L_q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This can pass f.i. into one of the osmotic equilibria:

$$L_c \mid Y + L_q \qquad X + L_e \mid L_q' \qquad L_p \mid L_g \quad . \quad . \quad . \quad (21)$$

in which L_q' is a liquid, represented by the point of intersection of the line Yq with the isotonic curve *e h*. In the first one of those equilibria the solid substance X has disappeared, therefore; in the second one the solid substance Y and in the last one as well X as Y.

The isotonic curves *a k* and *e h* divide the field of the unsaturated solutions into three parts, which behave differently with respect to the solid substances H and X. It follows from our previous considerations:

If we bring in osmotic contact the solid hydrate H or the solid substance X:

a. with a liquid of the field *akcb*, then the hydrate H remains unchanged, but the substance X flows away totally or partly;

b. with a liquid of the field *akeh*, then as well the hydrate H as the substance X flows away;

c. with a liquid of the field $ehWd$, then the hydrate H flows away totally or partly, but the solid substance X remains unchanged.

The three cases, mentioned above, occur only then, however, when the isotonic curve ak, starting in fig. 1 from point a, terminates in a point k between c and e and, therefore, does not intersect the saturation-curve de. We now imagine the point e anywhere between k and g; then the isotonic curve starting from a, intersects curve de in a point, which we shall call a_1. The isotonic curve starting from point e, will also then intersect the saturation-curve ab; this point of intersection, situated between a and f, is called e_1. We now find:

If we bring in osmotic contact the solid hydrate H or the solid substance X:

a'. with a liquid of the field $bcee_1$ then the hydrate remains unchanged, but the substance X flows away totally or partly;

b'. with a liquid of the field ee_1aa_1 then as well the hydrate as the solid substance X remain unchanged;

c'. with a liquid of the field aa_1dW, then the hydrate flows away totally or partly, but the solid substance X remains unchanged.

The field, mentioned above sub *b*, in which as well the hydrate as the solid substance X flow away, is replaced now by the field mentioned sub *b'*, in which as well the hydrate as the substance X remain unchanged.

The transition of field *b* into *b'* occurs when point e in fig. 1 coincides with point k; the two isotonic curves ak and he then coincide also. In this special case an osmotic equilibrium:

$$E = H + L_a \;\vdots\; X + L_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

can exist also. This is in accordance with the membrane-phase-rule. (Comm. VII and VIII). If we take constant the pressure of the two separate systems, an osmotic equilibrium has

$$n_1 + n_2 - (r_1 + r_2) + 1 - d$$

freedoms. The number of diffusing substances d is here: one; the number of components on each side of the membrane is two and also the number of phases. Consequently the number of freedoms is:

$$2 + 2 - (2 + 2) + 1 - 1 = 0.$$

Therefore, system (22) is invariant, consequently it exists only at a definite temperature and the composition of the two liquids is completely defined.

As is apparent from the situation of the saturation-curves bc and de in fig. 1 with respect to one another, we have assumed that the temperature, for which fig. 1 is valid, is higher than the eutectic temperature of the binary system XY. If we lower the temperature till below the eutectic and below the melting-point of ice, then we may obtain a diagram like fig. 2. Herein fg represents the ice-curve viz. the liquids saturated with ice, the $O.Y.A.$ of the liquids of this curve increases in the direction of the arrows viz. from f to g.

We now find for this fig. 2:

the $O.Y.A.$ of solid Y is equal to that of the liquids of the saturation-curve bc;

the $O.Y.A.$ of solid X is equal to that of solid $X + Y$, consequently also equal to that of the liquids of the saturation-curve bc;

the $O.Y.A.$ of the solid hydrate H is equal to that of the liquids of the isotonic curve al;

the $O.Y.A.$ of ice is equal to that of the liquids of the isotonic curve fo.

the $O.Y.A.$ of solid Y and of solid X is, therefore, smaller than that of all liquids of the field $abcdgf$.

It is apparent from the position of the isotonic curves in fig. 2 that a.o. the osmotic equilibria:

$$H + L_h \mid X + L_k \qquad H + L_a \mid X + L_l$$

$$H + L_b \mid X + Y + L_c \quad Ice + L_f \mid X + L_0 \quad Ice + L_p \mid X + L_q \qquad \text{fig. 2}$$

may occur now, which cannot exist in fig. 1.

We now take the osmotic system:

$$L_r \overset{|}{\rightarrow} L_s \qquad \text{fig. 2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

in which L_s has a greater $O.Y.A.$ than L_r, so that the substance Y in (23) diffuses in the direction of the arrow. Again it now depends on the ratio of the quantities of both the liquids, which will be the result of the diffusion. Two unsaturated liquids viz. can be formed, but (23) can pass also into the osmotic equilibrium:

$$Ice + L_r' \mid L_s' \quad \text{fig. 2} \; . \quad (24)$$

Herein L_r' is a liquid of the ice-curve, situated between the points f and p; L_s' is the point of intersection of the line Ys with the isotonic curve, which goes through the liquid L_r'.

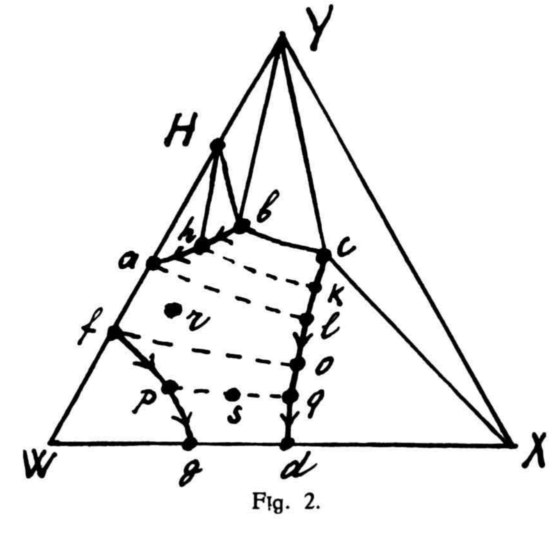

Fig. 2.

In the osmotic system:

$$Ice + L_p \leftarrow\!\!\mid H + L_h \text{ fig. 2} \quad \ldots \quad (25)$$

L_p has a greater $O.Y.A.$ than L_h; consequently the substance Y diffuses in the direction of the arrow. According to the composition of the liquids and the ratio of the quantities of the phases, there can arise from (25) a.o. the following osmotic equilibria:

$$Ys + L'_p \mid L'_h \qquad L''_p \mid H + L''_h \qquad L'''_p \mid L'''_h \quad \ldots \quad (26)$$

In the first one of those three equilibria L'_p is represented by a point p' of the ice-curve between p and f; L'_h is represented by a point h' viz. the point of intersection of the line YK, in which K represents the complex $H + L_h$, with the isotonic curve, starting from point p'. In a similar way we find the position of the points, which represent the liquids L''_p L''_h etc.

In the osmotic system:

$$Ice \mid L \qquad \text{fig. 2} \quad \ldots \quad (27)$$

it is dependent on the composition of the liquid L, whether diffusion of the substance Y will take place or not. The $O.Y.A.$ of the ice, as we have seen above, is equal to that of the liquid L_f, therefore, equal to that of the liquids of the isotonic curve fo.

Consequently if we take in (27) a liquid of the field $focba$, then the ice will melt totally or partly with formation of an unsaturated solution, consisting of water $+ Y$ or the solution L_f saturated with ice.

If, however, the liquid L in (27), is situated within the region $fodg$, then no Y diffuses towards the ice and the system rests unchanged, therefore.

If we bring in osmotic contact solid X with a liquid L, then we have the osmotic system:

$$X \mid L \qquad \text{fig. 2} \quad \ldots \quad (28)$$

As long as L is an unsaturated liquid, diffusion of Y can not occur in this system. If viz. a little Y diffuses, then at the left of the membrane the system $X + Y$ occurs, which has the same $O.Y.A.$ as the liquids of saturation-curve bc. As the $O.Y.A.$ of solid X is smaller, therefore, than that of every liquid of the field $abcdgf$ (fig. 2) this diffusion can not occur, therefore, and system (28) remains unchanged.

If L in (28) is a supersaturated liquid with respect to solid Y then, however, it is quite different. If f.i. this is situated in the field bcY, then its $O.Y.A.$ is smaller than that of the solid substance X and consequently (28) is converted into the osmotic equilibrium:

$$X + Y \mid L' \qquad \text{fig. 2} \quad \ldots \quad (29)$$

in which L' represents a saturated solution of curve bc.

Summarising some of the previous considerations, we may say:

Ice in osmotic contact with a liquid
of the field *fodg* remains unchanged;
of the field *focba* flows away totally or partly.

The hydrate *H* in osmotic contact with a liquid
of the field *alcb* remains unchanged;
of the field *aldgf* flows away totally or partly.

Solid *Y* in osmotic contact with every liquid of the total unsaturated field flows away totally or partly.

Solid *X* in osmotic contact with every liquid of the total unsaturated field remains unchanged.

(*To be continued.*)