Chemistry. — *Osmosis of ternary liquids, General considerations.* VII.
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Congruent and incongruent osmosis; the membrane.

In the preceding communication (Gen. VI) we have seen that there is a great difference in the behaviour of a membrane, transmitting only one substance and a membrane, transmitting more substances. We saw among other things:

a substance S diffuses through a membrane M (S) in congruent direction viz. from smaller towards larger $O. S. A.$;

a substance S can diffuse through a membrane $M\,(n)$ in both directions namely congruently or incongruently; it depends on the nature of the membrane which of these directions will occur.

We might express this in the following way:

a membrane, which transmits only one single substance, is "passive", a membrane, which transmits more substances, is "active" with respect to the direction in which a substance diffuses.

We shall refer to this later on.

The three isotonic curves, which in fig. 2 (Gen. VI) run through point 1 divide the triangle into six fields; we call these field p, field q, etc. in accordance with the points p, q etc. situated in these fields. The six osmotic systems:

$$\left.\begin{array}{lll} L_1 \mid L_p & L_1 \mid L_q & L_1 \mid L_r \\ L_1 \mid L_s & L_1 \mid L_t & L_1 \mid L_u \end{array}\right\} \quad \ldots\ldots \quad (1)$$

which we have discussed already in Gen. VI, we shall call system p, system q etc. The $D. T.$'s (diffusion-types) of each of these systems are found in scheme I (Gen. VI); in this scheme namely we have indicated for each separate system, which $D. T.$ is incongruent and, therefore, not possible. Consequently N⁰. 5 disappears in system p, N⁰. 6 in system q, N⁰. 2 in system r etc.

In the osmotic system

$$L_1 \mid L_p \quad \ldots\ldots\ldots\ldots \quad (2)$$

all $D. T.$'s, are possible except the incongruent one, viz. N⁰. 5. It appears, however, from the deduction that we have to take this "possible" only in the sense: from a thermodynamical point of view there is no objection to the occurrence of these seven *D. T.*'s. For this reason we shall call them: "admissible" *D. T.*'s.

Of course an infinite number of systems p must exist; we namely may imagine the right-side liquid p of (2) in any point of field p and besides in each of these systems different membranes. All these systems have the same incongruent *D. T.* N⁰. 5.

We now imagine in (2) a definite membrane and a definite liquid p; then also a definite *D. T.* will occur, e.g. N⁰. 4. When liquid p now travels through field p, then it may be that all these systems yet have the same *D. T.* N⁰. 4. Then only N⁰. 4 occurs of the seven "admissible" *D. T.*'s.

We can also imagine, however, that in one part of field p the *D. T.* N⁰. 4 obtains and in an other part e.g. N⁰. 3. Then only two of the seven "admissible" *D. T.*'s will occur.

If in (2) we now replace the membrane by another, we may imagine that e.g. the *D. T.* N⁰. 1, 2 and 4 will obtain.

From this it becomes clear that we can say:

The composition of the liquids determines which *D. T.* will be incongruent; which of the "admissible" *D. T.*'s will obtain, is not only determined by the composition of the liquids but also by the nature of the membrane.

These considerations now lead us to the question:

is it possible to find some further connection between the respective influences of the membrane and the composition of the liquids on the *D. T.*

Before we can enter upon a discussion of this question it will be first necessary to consider two more special cases of the osmosis.

A. We take the osmotic system:

$$\left.\begin{array}{ccc} & L \mid L' & \\ \longleftarrow \alpha X & \longleftarrow \beta Y & \longleftarrow \gamma W \end{array}\right\} \quad . \quad . \quad . \quad (3)$$

in which α mol. X, β mol. Y and γ mol. W diffuse in the direction of the arrows. If we take α, β and γ infinitely small, they will have to satisfy (comp. Gen. VI):

$$\alpha K_x + \beta K_y + \gamma K_w > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We now imagine the special case that both liquids of (3) have the same *O.W.A.*, then no water can possibly diffuse through a membrane $M(W)$. Is this also the case, however, when we take a membrane $M(XYW)$?

When the liquids have the same *O.W.A.* then $K_w = 0$; in (4) the last term will disappear and we get:

$$\alpha K_x + \beta K_y > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that γ now needs not satisfy a single condition; it is only necessary that α and β shall satisfy (5). Consequently (4) or (5) can be satisfied not only by $\gamma = 0$ but also by pos. and neg. values of γ.

So it is possible that a membrane $M(X\,Y\,W)$ exists, through which no W will diffuse; in general, however, water will diffuse and the nature of the membrane will determine in which direction it will go. Consequently we may say:

When two liquids have the same *O.W.A.*, then W does not diffuse through a membrane $M(W)$ but as a rule it does diffuse through a membrane $M(n)$.

As, however, (5) must be satisfied, both terms cannot be negative at the same time. This means (Comp. Gen. VI) that X and Y do not diffuse incongruently at the same time. So we find:

when two liquids have the same *O.W.A.*, then $n-1$ other substances cannot diffuse incongruently at the same time.

It is clear that the preceding is not only valid for the substance W, but for any substance S.

B. When the *O.X.A.*, *O.Y.A.* and *O.W.A* differ on both sides of the membrane, then there are seven "admissible" *D.T.*'s; there are transitiontypes between them, however, which occur when one of the substances does not happen to pass through the membrane, If e.g. N^0. 1 and N^0. 3 of scheme I are both "admissible" *D.T.*'s, then W diffuses

SCHEMA I

	X	Y	W
1.	⟵	⟶	⟵
2.	⟵	⟶	——
3.	⟵	⟶	⟶

in 1 towards the left and in 3 towards the right. Now we may imagine as a transition-state that the water diffuses neither towards the left nor to the right; we then get the transition *D.T.* N^0. 2, in which the arrow sub W has been replaced by a dash.

If in (4) we put $\gamma = 0$, so that this passes into (5), we see that the transition-*D.T.* is "admissible". Consequently we may say:

When two substances have a different *O.W.A.*, then W must always diffuse through a membrane $M(W)$, but not always through a membrane $M(n)$.

If accidentally W does not diffuse through a membrane $M(n)$, then the $n-1$ other substances cannot diffuse incongruently at the same time.

Of course the above also obtains for every substance S.

C. It appears among other things from the following remarks that the phenomena, discussed above, can really take place.

Experimentally (comp. Gen. VI) we have found that in a definite system the diffusion went through three different membranes according to

$D.\ T.$ N⁰. 1 of scheme I, but through three other membranes according to N⁰. 3. We can now imagine that there may be membranes, for which N⁰. 2 is valid.

We found the same thing for some other systems too (comp. Gen. VI).

We may find the transition-type also by changing not the membrane, but the composition of one or of both liquids.

We take e.g. the two systems:

$$L \mid L_a \qquad L \mid L_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which L_a and L_b have different compositions; they have the same L, however, and the same membrane. We now found (comp, Exp. I—III) that in the one system the diffusion took place according to N⁰. 1 and in the other system according to N⁰. 3 of scheme I. Consequently between L_a and L_b a liquid must be situated, for which the $D.\ T.$ N⁰. 2 (scheme I) obtains.

If we take an arbitrary osmotic system and leave it to itself, every liquid will travel along its path. Now it has been proved experimentally (Exp. I—III) that the $D.\ T.$ may change during the osmosis. On one part of the path e.g. N⁰. 1 is valid and on the other part N⁰. 3 of scheme I. So there is also a moment in which N⁰. 2 is valid and consequently no water diffuses.

Similar systems, viz. those in which one of the substances does not pass through the membrane, generally exist only for a single moment. Because of the diffusion of the other substances namely, the liquids change their compositions and this change is generally of a nature, that all substances will diffuse again at once.

D. It appears from the above that the diffusion of water (or another substance) will be different, when different membranes viz. $M(W)$ or $M(n)$ are used. We shall compare both cases with one another.

1. The membrane $M(W)$. When the membrane only transmits W, then it only depends on the $O.W.A.$ of the two liquids whether the water will diffuse or not and in which direction this will take place. The $O.W.A.$ of a liquid only depends on its composition; we have [comp. (6) Gen. VI]

$$O.W.A. = \xi_w = -\zeta + x\frac{\partial \zeta}{\partial x} + y\frac{\partial \zeta}{\partial y}.$$

With the aid of this we found;

I. when two liquids have the same $O.W.A.$, no W diffuses;

II. when two liquids have a different $O.W.A.$, W does diffuse;

III. W diffuses congruently viz. from smaller towards greater $O.W.A.$

2. The membrane $M(n)$. It appears from our considerations of systems, in which more substances pass through the membrane, that the rules I—III mentioned above do not obtain here. In A we have already

seen namely that W can indeed diffuse through a membrane $M(n)$, notwithstanding the $O.W.A.$ of both liquids is the same; consequently rule I is no longer valid.

In B we saw that sometimes no W diffuses through a membrane $M(W)$, notwithstanding the $O.W.A.$ of the two liquids is different, and in Gen. VI we have seen that a substance W can diffuse through a membrane $M(n)$ as well congruently as incongruently. Consequently the rules II and III are not valid any longer either.

So the $O.W.A.$ plays a direct part with a membrane, only transmitting W, but no more when at the same time other substances may diffuse also. Then the diffusion of the water not only depends on the $O.W.A.$ but also on the other diffusing substances and besides on the nature of the membrane.

We may assume, however, that a function exists, which plays a part with respect to the diffusion of W through a membrane $M(n)$ viz. the function ξ_w corresponding to that of the $O.W.A.$ with respect to the diffusion of W through a membrane $M(W)$.

We shall call this the $O.W.n.A.$ of a liquid; here the n indicates that n substances diffuse. This function, however, not only depends on the composition of the liquids, but, as it is valid for a membrane $M(n)$, also on the nature of the membrane. We shall refer to this when discussing the adsorption etc. of membranes.

We now choose this $O.W.n.A.$ in such a way that the diffusion of water through a membrane $M(n)$ we comply with:

I^n. when two liquids have the same $O.W.n.A.$, no W diffuses;

II^n. when two liquids have different $O.W.n.A.$, W does diffuse.

III^n. W diffuses from smaller towards greater $O.W.n.A.$

In connection with our previous considerations it is clear now:

a. when two liquids have the same $O.W.A.$, they generally will have a different $O.W.n.A.$:

b. when two liquids have a different $O.W.A.$, they may yet happen to have the same $O.W.n.A.$;

c. when a liquid p has a greater $O.W.A.$ than a liquid q, p may yet have a smaller $O.W.n.A.$ than q.

In A we have already seen namely that water can pass through a membrane $M(n)$ notwithstanding the liquids have the same $O.W.A.$; then they have a different $O.W.n.A.$ (comp. a.).

We saw in B that sometimes no water passes through a membrane $M(n)$ notwithstanding the liquids have a different $O.W.A.$; then they have the same $O.W.n.A.$ (comp. *b.*).

In Gen. VI we saw that water can diffuse through a membrane $M(n)$ from a liquid p towards q, notwithstanding p has a greater $O.W.A.$ than q; then the liquid p has a smaller $O.W.n.A$ than q (comp. c.).

When two liquids have the same $O.W.A.$ and consequently no water passes through a membrane $M(W)$, we call these "isotonic" with respect to W.

When two liquids have the same $O. W. n. A.$ and consequently no W passes through that same membrane $M(n)$, we shall call these "iso-n-tonic" or "isentonic" with respect to W.

It appears from the above:

when two liquids are isotonic with respect to W, they are generally not isentonic;

when two liquids are not isotonic with respect to W, then they may yet happen to be isentonic.

In Gen. VI we have deduced:

all liquids having the same $O. W. A.$ as a liquid g are situated on a curve $a\,b$, running through point g (comp. fig. 1 Gen. VI); we have called this an "isotonic W-curve".

We now may say also:

all liquids, which have the same $O. W. n. A.$ as a liquid g are situated on a curve going through point g; we call this the "isentonic W-curve".

It is clear and we shall refer to this later on that the isotonic and isentonic W-curves, running through the same point will generally vary a good deal.

All that has been said above for the diffusion of water obtains of course also for the diffusion of other substances; with the diffusion of an arbitrary substance S we then can speak of the $O. S. n. A.$ and the isentonic S-curve.

We shall see besides how these isentonic curves may serve us in order to get a better insight in the diffusion through a membrane $M(n)$.

E. We may deduce some results of this and preceding communications also in an other way. For this purpose we consider a system

$$L \mid L' \quad \ldots\ldots\ldots\ldots \quad (7)$$

in which two or more membranes have been placed between the liquids; we imagine them to lie at some distance from one another so that they can funtion independently from one another.

If in (7) we imagine two different membranes $M(S)$ then we may put the question:

Can the substance S diffuse through the one membrane towards the left and through the other towards the right?

If we assume this to be the case, then a current of S would arise in the system, running through the one membrane towards the left and through the other membrane towards the right; we call this a "circular current".

If the quantity of S, diffusing through these membranes, is different however, then both liquids change their compositions and at last the system comes in a state of equilibrium; the circular current of S has then stopped.

The surfaces of the membranes however may be treated in such a way that through the one as much S runs towards the left as through the other towards the right; then the liquids do not change their compositions and we get an eternal circular current of S. As we take, however, that this is not possible, we may conclude, therefore:

a substance S diffuses through all membranes $M(S)$ in the same direction.

Previously we have called this the congruent direction of S.

If in (7) we imagine a membrane $M(n)$ which transmits the substances X, Y, Z etc. we may put the question:

Can all these substances run through the membrane incongruently at the same time?

When the substance X diffuses incongruently, consequently in a direction opposite to the one through a membrane $M(X)$, we can regulate the surface of this membrane in such a way that as much X runs through $M(X)$ as through $M(n)$.

We are able to do the same for every incongruently diffusing substance, viz. for Y with a membrane $M(Y)$, for Z with a membrane $M(Z)$; etc.

When all substances diffuse incongruently, we have, therefore, a system in which at every moment as much X, Y etc. run through the membranes $M(X)$, $M(Y)$ etc., in congruent direction as through the membrane $M(n)$ in incongruent direction. Then the composition of the liquids would not change and we should have n eternal circular currents. So it follows from this:

all substances cannot diffuse incongruently at the same time; consequently the incongruent $D. T.$ is not admissible. We can also put the question:

Can the substances diffuse according to the congruent or to one of the mixed $D. T.$'s?

For every incongruently diffusing substance we may place a membrane transmitting the same quantity of this substance in congruent direction. As, however, we are not able to put an end to the diffusion of the congruently diffusing substances, the liquids consequently change their compositions, so we cannot get eternal circular currents now. From this point of view it follows in the same way as before:

the congruent and mixed $D. T.$'s are admissible.

When the diffusion through a membrane $M(n)$ takes place according to a mixed *D. T.*, we can alter this *D. T.* with the aid of an other membrane.

If one of the incongruently diffusing substances is e.g. water, we can do this with a membrane *M* (*W*) with such a surface that more *W* runs in congruent direction than in incongruent direction.

If we regulate the surface in such a way that the same quantity of *W* runs through both membranes, this combination of membranes functions, therefore, as a single membrane, through which no *W* diffuses in that moment. At that moment then the liquids are not "isotonic" but "isentonic" with respect to water; they then have not the same *O.W.A.* indeed but the same *O.W.n.A.*

(*To be continued*).

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