Chemistry. — *Osmosis of ternary liquids. General considerations* IV.
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The diffusing mixture and the diffusing liquid.

In communication III we have seen: if a liquid u proceeds along its osmosis-path $1 . e$ (fig. 1, Comm. II), then the other liquid u' proceeds along the path $1' . e$ and the diffusing mixture along a path, consisting of the two branches $1''a''$ and $a''e''$ (fig. 3, Comm. III). During the osmosis both liquids and the diffusing mixture change their compositions continuously; now we shall see in what way we may deduce the change of their quantities.

If at a moment t_1 there is n_1 quantities of L_1 on the left side of the membrane and on the right side n_1' quantities of L_1', we represent the system by:

$$n_1 \times L_1 \mid n_1' \times L_1' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At a moment t_2 this has passed into:

$$(n_1 - \triangle n) \times L_2 \mid (n_1' + \triangle n) \times L_2' \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the sake of concentration we imagine those liquids to be represented by the points 1, 1′, 2 and 2′ of fig. 2 (Comm. III). Consequently we have assumed, as it appears from (1) and (2), that $\triangle n$ quantities of the mixture s have diffused from left to right in the time $\triangle t = t_2 - t_1$.

If we consider the liquids on the left side of the membrane, we see that n_1 quantities of L_1 pass into $(n_1 - \triangle n)$ quantities of L_2 by giving $\triangle n$ quantities of L_s. We may write, therefore:

n_1 quant. of $L_1 - \triangle n$ quant. of $L_s = (n_1 - \triangle n)$ quant. of L_2.

We can also substitute for this:

n_1 quant. of $L_1 = \triangle n$ quant. of $L_s + (n_1 - \triangle n)$ quant. of L_2.

Consequently we can get the liquid L_1 by bringing together L_s and L_2 in the ratio $\triangle n : (n_1 - \triangle n)$. From this follows that point 1 must divide the line $s . 2$ into the parts $1 . s$ and $1 . 2$ which satisfy:

$$1 . s : 1 . 2 = (n_1 - \triangle n) : \triangle n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From this it follows:

$$\triangle n = \frac{1 . 2}{1 . s + 1 . 2} \times n_1 = \frac{1 . 2}{s . 2} \times n_1 = a\, n_1 \quad . \quad . \quad . \quad . \quad (4)$$

In order to given this a different form, we represent the composition of the mixture s by:

$$x_0 \text{ quant. of } X + y_0 \text{ quant. of } Y + (1 - x_0 - y_0) \text{ quant. of } W.$$

In order to represent the liquids 1 and 2, we substitute the index 0 by 1 and 2. In fig. 2 (Comm. III) we now imagine the sides WX and WY to be drawn and the coordinates of the points 1, 2 and 3.

Then we find:

$$1.2 : s.2 = (x_2 - x_1) : (x_2 - x_0) = (y_2 - y_1) : (y_2 - y_0).$$

From this follows:

$$\triangle n = a\, n_1 = \frac{1.2}{s.2} \times n_1 = \frac{x_2 - x_1}{x_2 - x_0} \times n_1 = \frac{y_2 - y_1}{y_2 - y_0} \times n_1 \quad . \quad . \quad (5)$$

So if we know the quantity n_1 of the liquid, which at the moment t_1 is on the left side of the membrane, we know also the quantity $\triangle n$, which has diffused through the membrane in the time $\triangle t = t_2 - t_1$. If $\triangle n$ is positive, then this quantity has diffused towards the right side, if $\triangle n$ is negative, then this quantity has diffused towards the left side.

It also follows from this how much of each of the substances has diffused through the membrane in this time $\triangle t$. We find:

$$\left.\begin{array}{ll} x_0 \triangle n = \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1\, x_0 = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1\, x_0 & \text{quant. of } X \\[2ex] y_0 \triangle n = \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1\, y_0 = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1\, y_0 & \text{quant. of } Y \\[2ex] \text{and } \dfrac{x_2 - x_1}{x_2 - x_0} \times n_1 (1 - x_0 - y_0) = \dfrac{y_2 - y_1}{y_2 - y_0} \times n_1 (1 - x_0 - y_0) & \text{quant. of } W \end{array}\right\} \quad . \quad (6)$$

A positive quantity has diffused towards the right side, a negative quantity towards the left side.

From (5) we can among other things deduce the following: if the diffused mixture is situated at infinite distance, then the quantity $\triangle n$, which has diffused in the time $\triangle t = t_2 - t_1$ through the membrane, is zero.

This becomes clear at once if we increase x_0 (or y_0) in (5) infinitely.

We must not think now, however, that in the time $\triangle t$ nothing has gone through the membrane. If in (6) e.g. x_0 and y_0 are taken infinitely large, we find:

$$\left.\begin{array}{c} x_0 \triangle n = (x_1 - x_2)\, n_1 \qquad y_0 \triangle n = (y_1 - y_2)\, n_1 \\ (1 - x_0 - y_0) \triangle n = (x_2 + y_2 - x_1 - y_1)\, n_1 \end{array}\right\} \quad . \quad . \quad (7)$$

which can also be very simply deduced in other ways. It now appears from (7) that in the time $\triangle t$ substances have indeed gone through the membrane, but that their total quantity is zero. Consequently we find:

if in the time $\triangle t$ a quantity p of the one substance and a quantity q of the other substance diffuses towards the right (or left) side, then in the same time a quantity $p+q$ of the third substance goes in opposite direction.

Consequently we have at the moment t_2 the same quantity of liquid on both sides of the membrane as at the moment t_1; in general, however, the volume will be different at the moments t_1 and t_2: the liquids have namely an other composition at the moments t_2 and t_1 respectively.

In order to find out what passes through the membrane in the infinitely small time dt, we imagine the points 2 and 2′ in the immediate vicinity of 1 and 1′; then we have:

$$x_2 = x_1 + dx_1 \qquad y_2 = y_1 + dy_1$$

If we substitute these in (5) and omit the index 1, it follows:

$$dn = an = \frac{dx}{x-x_0} \times n = \frac{dy}{y-y_0} \times n \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The infinitely small quantity dn which passes through the membrane in the infinitely small time dt is, therefore, defined by (8). Instead of (6) we find:

$$\left.\begin{array}{lr} x_0\, dn = \dfrac{dx}{x-x_0} \times n\, x_0 = \dfrac{dy}{y-y_0} \times n\, x_0 & \text{quant. of } X \\ y_0\, dn = \dfrac{dx}{x-x_0} \times n\, y_0 = \dfrac{dx}{y-y_0} \times n\, y_0 & \text{quant. of } Y \\ \text{and } \dfrac{dx}{x-x_0} \times n\,(1-x_0-y_0) = \dfrac{dy}{y-y_0} \times n\,(1-x_0-y_0) & \text{quant. of } W \end{array}\right\} \; . \quad (9)$$

The infinitely small quantities of the substance, which pass through the membrane in the time dt, are, therefore, defined by (9). If we take x_0 and y_0 infinitely large here, we find the same things as we have deduced above for the diffused mixture.

Consequently we may say:

If two conjugated tangents (or chords) of the osmosis-path run parallel and the diffusing (or diffused) mixture is situated, therefore, at infinite distance, then two of the substances diffuse in one direction through the membrane and a corresponding quantity of the third substance in the opposite direction.

In communication III we have seen: if a liquid u passes along the path $1 . e$ of fig. 1 (Comm. II), then the diffusing mixture u'' proceeds along a path, consisting of the branches $1''a''$ and $a''e''$ of fig. 3 (Comm. III). In scheme 11 (Comm. III) we find the direction indicated in which the diffusing mixture and each of the substances pass through the membrane. If we add to this what we are going to discuss further as regards the points *a*, *b* and *c*, we get scheme (10).

		L_s	X	Y	W
1.2.*m a*	IV	$\longrightarrow$	$\longleftarrow$	$\longrightarrow$	$\longrightarrow$
a	∞	0	„	„	„
a b	VII	$\longleftarrow$	„	„	„
b	*XY*	„	„	„	0
b 3 *c*	VI	„	„	„	$\longleftarrow$
c	*XW*	„	„	0	„
c 4 *e*	I	„	„	$\longleftarrow$	„

. (10)

If liquid u is in point a of its path, then u'' is, therefore, in point a'' which is situated at infinite distance; so the quantity of the diffusing mixture is zero; this is indicated in scheme (10) by the symbol ∞ and the figure 0. At this moment the substances Y and W diffuse towards the right side and a corresponding quantity of X towards the left side.

If liquid u is in point c, then u'' is in point c'' on side WX (fig. 3. Comm. III); the diffusing mixture, therefore, only contains the substances W and X so that no Y diffuses; this has been indicated in scheme (10) by the figure 0. It is apparent from this scheme: if liquid u travels along its path, then Y diffuses:

towards the right side, when u is situated between 1 and c
towards the left side, when u is situated between c and e

but in point c, Y does not diffuse.

If liquid u is in point b and, therefore, u'' in point b'' on side XY, then only the substances X and Y will diffuse; substance W does not diffuse. It now appears from scheme (10) if liquid u travels along its path, then W diffuses:

towards the right side, if u is situated between 1 and b,
towards the left side, if u is situated between b and e,

but in point b the substance W does not diffuse.

We shall now consider the osmotic systems:

$$L_2 \mid L_2' \qquad L_b \mid L_b' \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

of fig. 1 (Comm. II). In the former, which we have already discussed in our previous communications, both liquids have the same amount of W. It now appears from scheme (10):

in the first of these systems the substance W diffuses through the membrane, although both liquids have the same amount of W;

in the second system no W diffuses through the membrane, although both liquids have a different amount of W.

In order to represent the concentrations of the liquids during the osmosis, we have in communication II in the figs. 2, 3 and 4 drawn the time on the horizontal axis and on the vertical axis in fig. 2 the X-amount, in fig. 3 the Y-amount and in fig. 4 the W-amount.

We now can do the same for the diffusing mixture and besides indicate at the same time also in which direction the substance passes through the membrane. The axis Ot (fig. 1) namely divides the diagram into two parts; we shall draw the amount in the higher part (in which the arrow $\rightarrow$) when the substance diffuses towards the right side, and in the lower part (in which the arrow $\leftarrow$) when the substance diffuses towards the left side.

We shall begin by considering the Y-amount. If liquid u passes along the part $1 . a$ of its path in fig. 1 (Comm. II), then the diffusing mixture u'' passes along the path $1'' a''$ of fig. 3 (Comm. III). It appears from scheme (10) that the substance Y diffuses towards the right side in all points of this branch; consequently in fig. 1 we must draw the whole of branch $1'' a''$ above the axis Ot. It appears from fig. 3 (Comm. III)

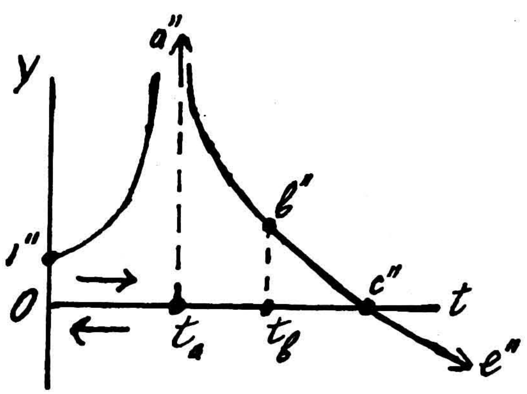

Fig. 1.

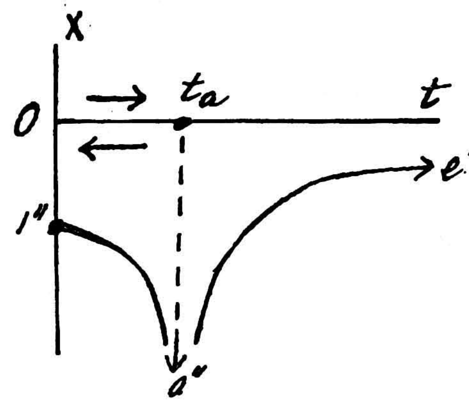

Fig. 2.

that the Y-amount increases starting from point $1''$ till in a'' where it becomes infinitely large. Therefore, in fig. 1 this branch must start from a point $1''$ on the Y-axis towards a point a'' which is situated at infinite distance on the line which goes through point t_a and runs parallel to the Y-axis.

When liquid u passes along the part $a\,b\,c\,e$ of its path, then u'' must pass along the branch $a''\,b''\,c''\,e''$ of fig. 3 (Comm. III). It appears from scheme (10) that the substance Y diffuses towards the right side on part $a''\,c''$ and towards the left side on part $c''\,e''$; consequently in fig. 1 the part $a''\,c''$ must be situated above the axis Ot and part $c''\,e''$ below that axis.

As the final liquid e, however, is not reached, until after an infinitely long time, we must, therefore, imagine e'' at infinite distance.

Consequently we see in fig. 1 not only the same in scheme (10) namely the direction in which the substance Y passes through the membrane at any moment, but also in what manner the Y-amount changes continually, If we imagine these curves of fig. 1 drawn also in fig. 3 (Comm. II) then, this figure will represent all changes, occurring during the osmosis in both liquids and in the diffusing mixture.

It is clear now that we can represent the W-amount also by two curves; we then find a similar diagram as fig. 1; the curve $a''e''$, however, now intersects the axis Ot in the point t_b, so that the part $b''c''e''$ is now situated below the axis Ot.

The X-amount is represented in fig. 2. Herein we also find two curves, which are both situated, however, below the axis Ot, as, during the total osmosis the substance X diffuses towards the left side.

We assume that in a time dt
α quantities of X diffuse towards the left side and β quantities of $Y + \gamma$ quantities of W towards the right side; α, β and γ are infinitely small and positive.

Consequently we may say that $(-\alpha + \beta + \gamma)$ quantities of the diffusing mixture have passed through the membrane towards the right side in the time dt. Of course we may say also that $(\alpha - \beta - \gamma)$ quantities of this mixture go towards the left side.

If, however, we only pay attention to the quantity, passing through the membrane, no matter whether the substances diffuse towards the right or towards the left side, then during this time dt

$$(\alpha + \beta + \gamma) \quad \text{quantities}$$

of substance namely $X + Y + W$ pass through the membrane in all. We then may say that $(\alpha + \beta + \gamma)$ quantities of a liquid of the composition:

$$\frac{\alpha}{\alpha+\beta+\gamma}\text{ quant. of } X + \frac{\beta}{\alpha+\beta+\gamma}\text{ quant. of } Y + \frac{\gamma}{\alpha+\beta+\gamma}\text{ quant. of } W$$

pass through the membrane.

We shall call this the "diffusing liquid".

Consequently there is a difference between the diffusing mixture and the diffusing liquid. The first, namely, indicates the composition of that which passes through the membrane, if we take into consideration not only the quantities but also the direction of the diffusion. In it the concentrations can have all values varying between $+\infty$ and $-\infty$, if only their sum be 1. The diffusing liquid, however, indicates the composition of that which passes through the membrane, if we do not take into consideration the direction of the diffusion, but if we add the diffusing quantities, no matter in which direction they pass through the membrane. Consequently the concentrations are all positive and smaller than 1.

Therefore, the diffusing liquid is a real liquid, namely a liquid which we can compose of the three liquids.

This is also the case with the diffusing mixture, if this is situated in field I (consequently within triangle WXY). If it is situated, however, in one of the other fields, so that one or two of the concentrations are negative, then it is an imaginary liquid, namely a liquid which cannot exist in reality. For this reason we have called it "mixture" instead of liquid.

If we know the quantity dn and the composition:

$$x_0 \text{ quant. of } X + y_0 \text{ quant. of } Y + (1 - x_0 - y_0) \text{ quant. of } W.$$

of the mixture, which diffuses through the membrane in the time dt, then we can deduce from this the quantity and the composition of the diffusing liquid. If e.g. the mixture is situated in field IV then x_0 is negative; y_0 and $1-x_0-y_0$ are positive. We now put $x_0 = -p$ and $y_0 = q$ so that p and q are positive. Then the mixture becomes:

$$-p \text{ quant. of } X + q \text{ quant. of } Y + (1 + p - q) \text{ quant. of } W.$$

In the time dt, therefore, $p \,.\, dn$ quantities of X go through the membrane in the one direction and $q\, dn$ quantities of $Y + (1 + p - q)$ quant. of W go in opposite direction through the membrane. Consequently:

$$p \,.\, dn + q \,.\, dn + (1 + p - q)\, dn = (1 + 2\,p)\, dn$$

quantities of liquid pass through the membrane in all; the composition of this liquid is:

$$\frac{p}{1+2p} \text{ quant. of } X + \frac{q}{1+2p} \text{ quant. of } Y + \frac{1+p-q}{1+2p} \text{ quant. of } W.$$

If the mixture is situated in field VII, then y_0 and $1 - x_0 - y_0$ are negative. We now put $x_0 = p > 1$ and $y_0 = -q$. Consequently the mixture has the composition:

$$p \text{ quant. of } X - q \text{ quant. of } Y - (p - q - 1) \text{ quant. of } W.$$

We now find that $(2\,p - 1)\, dn$ quantities of liquid of the composition:

$$\frac{p}{2\,p-1} \text{ quant. of } X + \frac{q}{2\,p-1} \text{ quant. of } Y + \frac{p-q-1}{2\,p-1} \text{ quant. of } W$$

pass through the membrane.

If the mixture is situated in field VI then only y_0 is negative. We now put $x_0 = p < 1$ and $y_0 = -q$. Then the mixture has the composition:

$$p \text{ quant. of } X - q \text{ quant. of } Y + (1 - p + q) \text{ quant. of } W.$$

It follows from this that $(1 + 2\,q)\, dn$ quantities of liquid of the composition:

$$\frac{p}{1+2\,q} \text{ quant. of } X + \frac{q}{1+2q} \text{ quant. of } Y + \frac{1-p+q}{1+2\,q} \text{ quant. of } W$$

pass through the membrane.

In a corresponding way we find the quantity and composition of the diffussing liquid, when the diffusing mixture is situated in one of the other fields.

What has been discussed above is of course also valid for the diffused mixture and the diffused liquid.

If liquid u passes along its path $1 \cdot e$ of fig. 1 (Comm. II), then the diffusing mixture u'' passes along the branches $1''a''$ and $a''e''$ of fig. 3 (Comm. III); the X-, Y- and W-amount of this mixture u'' is represented in the figures 1 and 2. In a corresponding way we can also represent the diffusing liquid.

We now shall unite the three curves in one diagram (fig. 3); in order not to make the figure too large, however, we are now going to use only the higher part. In order yet to indicate in which direction a substance passes through the membrane, we shall draw that part of the curve, on which the substance diffuses towards the right side, in full, but we shall dot the part on which the substance diffuses towards the left side.

In fig. 3 these directions are represented by an arrow fully drawn and by a dotted arrow.

As all concentrations of the diffusing liquid are now situated between 0 and 1, the curve in fig. 3 will have quite another form from those in figs. 1 and 2.

In fig. 3 the X-amount is represented by the curve, near which the letter X has been put. The starting-point $1''$ is of course situated on the axis OC and the final-point e'' at infinite distance. As the substance X diffuses towards the left side during all the osmosis, this curve has been dotted.

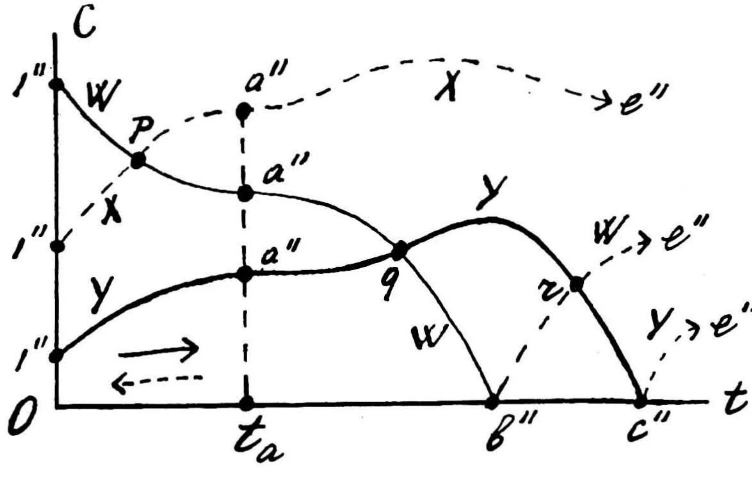

Fig. 3.

The Y-amount is represented by the curve near which the letter Y has been put. We see in scheme (10) that the Y-amount of the diffusing mixture, and consequently also that of the diffusing liquid, is zero in point c; consequently the curve must at the moment t_c come in the point c'' on the axis Ot. As on the part $1''c''$ the substance Y diffuses towards the right side and on $c''e''$ towards the left side (comp. scheme

10), the first part, therefore, has been drawn in full and the second part has been dotted.

The W-amount is represented by the curve near which the letter W has been put. It appears from scheme (10) that at the moment t_b it must come in a point b'' of the axis Ot and that the part $1''b''$ should be drawn in full and the part $b''e''$ must be dotted.

Although from a theoretical point of view little can be said as yet as to the shapes etc. of those curves; we may yet deduce a few properties.

In the first place it is clear that we always know one of those curves, when the other two are known. Somewhere on the axis Ot we imagine a point z; the perpendicular in z intersects each of the three curves in a point, we shall call z''. As each of these lines zz'' represents a concentration and as the sum of the three concentrations is 1, the sum of these three lines zz'' must, therefore, always be 1. The reader will probably not object that in drawing this sketch-figure we have not paid sufficient attention to this.

Previously we have already deduced that in point a'' the substances Y and W diffuse towards the right side and a corresponding quantity of X towards the left side (compare also scheme 10). Consequently in fig. 3 the longest line $t_a\,a''$ must, therefore, be as long as the sum of bot the other lines $t_a\,a''$; consequently it is $^1/_2$.

We can show besides that the curves have a horizontal tangent in a''.

The X- and W-curves intersect one another in point p; consequently at that moment as much X as W passes through the membrane; the X goes towards the left side and the W towards the right side.

The Y- and W-curves intersect one another in the points q and r. Consequently in q as much Y as W passes through the membrane towards the right side; in r as much Y goes towards the right side as W towards the left side.

These points of intersection correspond with definite points of fig. 3 (Comm. III). We can easily deduce:

in fig. 3 (Comm. III) point p is the point of intersection of branch $1''a''$ with the horizontal line, which is drawn through point Y;

point q is the point of intersection of branch $a''e''$ with the bisectrix of angle WXY;

point r is the point of intersection of branch $a''e''$ with the vertical line, which passes through point X.

(To be continued).

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